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# **The Role of Polymer Flocculants in Microfiltration of Surface Water**

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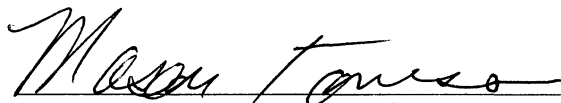
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# **Abstract**

## **The Role of Polymer Flocculants in Microfiltration of Surface Water**

by

Sen Wang

Polymer flocculants, traditionally used with primary coagulant to enhance flocculation and sedimentation, are used in the coagulation/microfiltration process as well assuming they can improve membrane performance similarly. However, there are several uncertainties concerning the use of polymer flocculants in the coagulation-microfiltration process. First, polymer flocculants may not have measurable effect on turbidity removal, because microfiltration membranes can remove significantly smaller particles than those removed by the conventional treatment process. Second, the effect of using polymer flocculants on NOM removal has been controversial. Although a number of studies reported improved NOM removal when polymers were used, others reported no or negative impact of polymers on NOM removal. Third, polymer flocculants are high molecular weight organic compounds. When carried over to membrane residual polymers can potentially foul the membranes. Finally, the use of polymer flocculants will change floc properties (i.e. size, fractal dimension, and stickiness) and subsequently bring uncertain effect on cake layer resistance. Therefore, the role of polymer flocculants in coagulation-microfiltration system needs to be carefully assessed for system optimization. In the reported research, three types of polymer flocculants with different charge and molecular weights were tested for comprehensively evaluating the impact of

polymer flocculants on the performance of coagulation-microfiltration of surface water. Operation conditions such as inline filtration, direct filtration, and filtration with sedimentation were included. Two membrane reactors were designed to study the mechanism through which polymer flocculants affect the performance of coagulation-microfiltration systems. The result demonstrated that the use of polymer flocculants provides little to no benefit to turbidity and NOM removal in most cases, but pDADMACs can enhance NOM removal if applied properly; All polymer flocculants significantly increased membrane fouling except for pDADMACs when sedimentation proceeds MF; Polymer flocculants increase deposition/attachment of floc particles on the membrane surface through both adsorption of residual polymer on the membrane surface and polymer molecules on the floc particle surface; Even though polymers form larger and more fractal floc particles, they did not have notable impact on cake layer structure.

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# ***Chapter 1 Introduction and Research Objectives***

## 1.1. Introduction

Drinking water treatment for public health is of vital importance throughout the world, because many illnesses and even deaths can be caused by contaminations such as pathogens, suspended and dissolved matters. As a relative new treatment process emerged in recent decades, microfiltration for drinking water treatment is experiencing a significant increase in application world widely due to its smaller footprint, superior treated water quality, and higher level of automation compared to conventional treatment processes. Major limitations of the microfiltration technology include the inefficiency in natural organic matter (NOM) removal (Vickers et al., 1995) and membrane fouling. Many source waters contain significant amount of NOM — a precursor of harmful disinfection byproducts. In addition, membranes can be fouled by NOM over time, leading to a loss of production and requiring more frequent cleaning. As a result, coagulation using hydrolyzing metal salts is often used as pretreatment for microfiltration to increase NOM removal and to control membrane fouling.

Polymers are widely employed in the coagulation/flocculation process in conventional water treatment systems (Bolto and Gregory, 2007). They are known to improve effluent water quality by increasing floc size and strength, reduce alkalinity consumption, and alleviate sludge handling and disposal problems (Gray and Ritchie, 2006, Jin et al., 2003, Taylor et al., 2002, Zhao, 2004). Polymers are adopted in the coagulation/flocculation pretreatment process as well in many microfiltration systems (Nozic et al., 2001) assuming that they would improve the performance of the coagulation-MF process through the same mechanisms as in the conventional treatment

process. However, there are several uncertainties concerning the use of polymer flocculants in the coagulation-microfiltration process. First, polymer flocculants may not have measurable effect on turbidity removal, because microfiltration membranes can remove significantly smaller particles than those removed by the conventional treatment process. Second, the effect of using polymer flocculants on NOM removal has been controversial. Although a number of studies reported improved NOM removal when polymers were used (Jarvis et al., 2008b, Kim and Walker, 2001, Lee and Westerhoff, 2006), others reported no or negative impact of polymers on NOM removal (Chang et al., 2005, Jarvis et al., 2006). Third, polymer flocculants are high molecular weight organic compounds. When carried over to membrane residual polymers can potentially foul the membranes. Finally, the use of polymer flocculants will change floc properties (i.e. size, fractal dimension, and stickiness) and subsequently bring uncertain effect on cake layer resistance. Therefore, the impact of polymer flocculants on membrane performance in coagulation-microfiltration system needs to be carefully assessed for system optimization.

## **1.2. Research Objectives**

The objective of this research is to systematically investigate the role of polymer flocculants in coagulation-microfiltration of surface water. Specifically, this research aims at addressing the following three questions: (1), can the microfiltration membrane be fouled when excessive polymer flocculants when primary coagulant is used? (2), what is the impact of polymer flocculants on the performance of membrane microfiltration of

surface water including contaminant removal and membrane fouling? (3), what are the mechanisms behind polymers' impacts on the coagulation-microfiltration system performance?

The dissertation contains nine chapters. Chapter 2 of the dissertation presents a literature review for microfiltration, coagulation, and polymer flocculants. Chapter 3 describes the methodologies used in this research. Chapter 4 shows the investigation of the fouling of microfiltration membrane by free polymers. Chapter 5 presents the impact of polymer flocculants on coagulation pretreatment. Chapter 6 demonstrates the impact of polymer flocculants on the performance of microfiltration. Chapter 7 tries to illustrate the mechanisms of polymer flocculants' impact on membrane microfiltration performance. Chapter 8 concludes the dissertation, and Chapter 9 listed the unsolved problems that need further investigation in the future.

## ***Chapter 2 Literature Review***



## **2.1. Microfiltration**

### **2.1.1. Membrane Filtration**

Membrane filtration is an emerging technology with rapid development and widespread application. Membrane could be defined as “*a selective barrier between two phases with the term ‘selective’ being inherent to a membrane or a membrane process*” (Moulder, 2003). Membranes can be gaseous, liquid, and solid or combinations of these. Membranes can also be (1) natural or synthetic; (2) porous or nonporous; (3) used for gaseous phase separation, gas-liquid separation or liquid-liquid separation; (4) adsorptive, diffusive, ion-exchange, osmotic, or nonselective (inert) (Munir, 1998). Table 2-1 lists various membrane processes in the water treatment field with corresponding characteristics such as driving force, retentate, and permeate.

Table 2-1 Characteristics of different membrane processes

Process	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Driving Force	Pressure	Pressure	Pressure	Pressure
Retentate	Suspended Particles, water	Large molecules,	Small molecules, Divalent salts, Disassociated acids, Water	All solutes, Water
Permeate	Dissolved solutes, water	Small molecules, Water	Monovalent ions, Undisassociated acids, water	Water
Process	Electrodialysis	Pervaporation	Osmosis	Dialysis
Driving Force	Voltage/Current	Pressure	Chemical Potential	Concentration Difference
Retentate	Nonionic solutes, water	Nonvolatile solutes, water	Solutes, Water	Large Molecules, water
Permeate	Ionized solutes, Water	Volatile small solutes, Water	Water	Small molecules, water

Source: (Munir, 1998)

### 2.1.2. Microfiltration

Microfiltration (MF) is a process that removes contaminants from a fluid by passing through a micro porous membrane (Crittenden et al., 2005). A typical range of microfiltration membrane pore size is 0.1 to 1  $\mu\text{m}$ . For comparison, the application range of microfiltration is presented together with ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) in Figure 2-1 (Christensen, 2005).

	Ionic Range		Molecular Range		Macro molecular Range	Micro particle Range	Macro particle Range	
Size, $\mu\text{m}$	0.001		0.01	0.1	1.0	10	100	1000
Molecular Weight Approx.	100	1000	100,000	500,000				
Relative Sizes	Dissolved Salts (Ions)		Virus		Bacteria			
	Organics (e.g. color)				Algae			
				Clays	Crysts		Sand	
					Silts			
					Asbestos Fibers			
Separation Process	Reverse Osmosis	Ultra Filtration		Micro Filtration	Conventional Filtration (Granular Media)			
		Nano Filtration						

Figure 2-1 Application range of various membranes

The main applications of microfiltration include sterilization (food and pharmaceuticals), ultrapure water (semiconductors), clarification (beverages), cell harvesting and membrane bioreactor (biotechnology), plasmapheresis (medical), and water treatment (Moulder, 2003).

Microfiltration can be operated in two different modes: dead end and cross-flow as depicted in Figure 2-2. In dead end filtration, source water flows perpendicularly to the microfiltration membrane; foulant will be rejected and accumulated on the membrane surface bringing a loss of permeate flux. In cross flow filtration, the source water flows parallel to the membrane surface while permeating through the membrane, generating a permeate and a concentrated retentate stream at the same time. Because the cross-flow mode requires many times more energy than the dead-end mode, mostly used for flow



circulation, dead end filtration is usually favored. Therefore, dead-end filtration is always used when the solid content is lower than 0.1%; however, cross flow is needed when the fluid solid content is too high (e.g. 0.5%) to avoid severe fouling of the membrane (Baker, 1991).

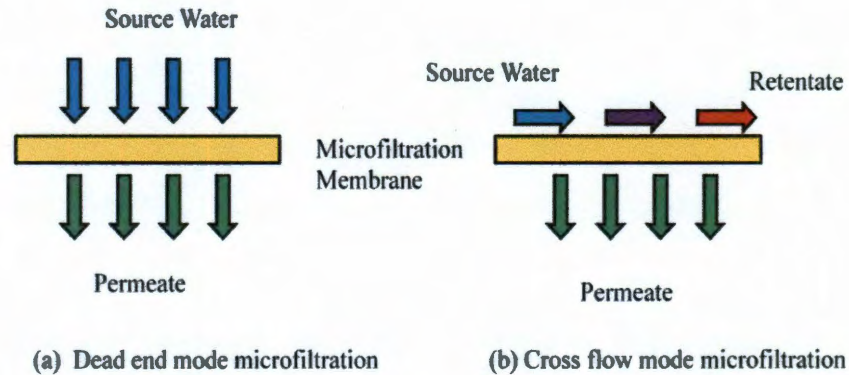


Figure 2-2 Schematics of dead end and cross flow mode microfiltration

Several important parameters are usually used to characterize membrane filtration process: rejection, recovery, and permeability, which are defined in equations 2-1, 2-2, and 2-3 respectively.

$$R = 1 - \frac{C_p}{C_f} \quad \text{Eq. 2-1}$$

Where:

R is observed rejection

$C_p$  is solute concentration in the permeate;

$C_f$  is solute concentration in the feed.

$$R_0 = \frac{Q_p}{Q_f} \quad \text{Eq. 2-2}$$

Where:

$R_0$  is recovery;

$Q_p$  is permeate flux,  $\frac{m^3}{s}$ ;

$Q_f$  is feed flux,  $\frac{m^3}{s}$ .

$$J = \frac{\Delta P}{\mu R_m} = L_p \Delta P \quad \text{Eq. 2-3}$$

Where:  $J$  is clean water flux of the membrane,  $\frac{m^3}{m^2 \cdot s}$ ;

$\Delta P$  is transmembrane pressure, psi;

$L_p$  is membrane permeability,  $\frac{m}{s \cdot psi}$ ;

$R_m$  is membrane resistance,  $m^{-1}$ .

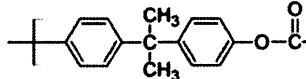
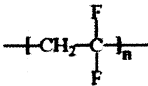
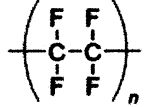
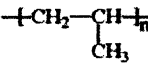
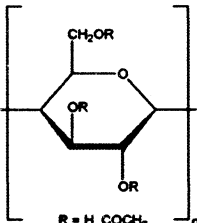
### 2.1.3. Microfiltration Membrane Materials

MF membranes can be manufactured with various materials including polymers, ceramics (Bottino et al., 2001), and metals (Agoudjil and Benkacem, 2007, Agoudjil et al., 2005, Karnik et al., 2005a, 2005b, Leiknes et al., 2004). Polymeric and ceramic membranes are the only two materials for membranes used in water treatment field. Because polymeric membranes have several advantages compared to ceramic membranes such as low cost, easy to scale up, and easy variation in module form (DrIoli and Giorno, 2009), they are the most commonly used MF membranes in water treatment. Ceramic membranes have longer life time, excellent chemical resistance, thermal stability, and they are thermally regenerable from used membranes (DrIoli and Giorno, 2009). Therefore, they are widely used in chemical processing.

Common polymer materials for MF membranes are listed in Table 2-2 together with their molecule structures. Polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), and isotactic polypropylene (PP) are hydrophobic and not soluble in common

solvents; membranes made of these materials especially PTFE have good thermal and chemical resistance. However, stable hydrophilic polymers are attractive because membranes made of these materials have lower adsorption capacity and fouling tendency. Cellulose and its derivatives such as cellulose esters are popular hydrophilic materials for not only microfiltration membrane but also ultrafiltration and reverse osmosis membranes. Polyamide is another commonly used membrane material. Polyamide polymers can be either aliphatic or aromatic group. Aromatic polyamides are usually preferred because of their exceptional mechanical, thermal, chemical and hydrolytic stability (Moulder, 2003).

Table 2-2 Common polymers for microfiltration membranes

Polymers	Chemical structure
Polycarbonate	
Poly(vinylidene-fluoride) (PVDF)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	
Polyamide	NA
Cellulose-esters	

Source: (Moulder, 2003)

#### 2.1.4. Application of Microfiltration in Drinking Water Treatment

Although the earliest research about MF can be traced back to the middle of the twentieth century (Goldberg et al., 1952), studies on application of microfiltration in drinking water treatment did not start late 1980s (Treffrygoatley et al., 1987). Around the same time, MF was introduced to the municipal water treatment market by two companies: Aquasource in France and Memcor in Australia (Christensen, 2005). In the United States, the 1996 Safe Drinking Water Act Amendments, which requires lower treated water turbidity and removal of disinfectant resistant bacteria such as *Giardia* and *Cryptosporidium*, triggered the momentous development of the MF technology in both academia and industry (Christensen, 2005).

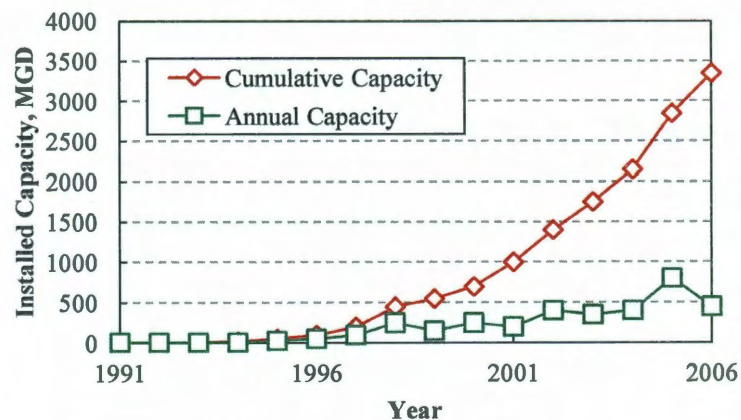


Figure 2-3 Global low pressure membrane installed capacity (Furukawa, 2008)

The past few decades saw rapid growth in the application of low pressure membranes (MF and UF). In 2006, the global cumulative installed capacity of low pressure membranes reached ~3500 million gallon per day (MGD) as shown in Figure 2-



3 (Furukawa, 2008). Among the different applications of low pressure membranes, drinking water treatment occupied 60 % of the global market (Figure 2-4).

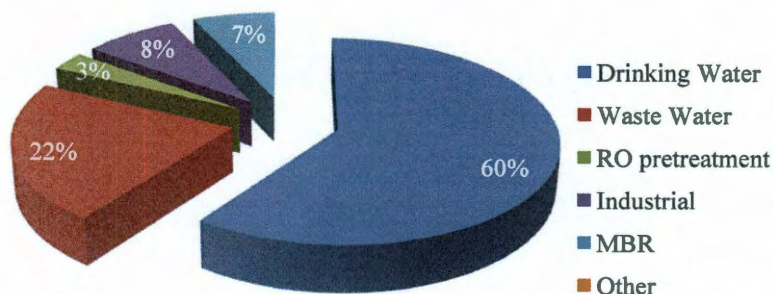


Figure 2-4 Global low pressure membrane installation by application (Furukawa, 2008)

### 2.1.5. Characterization of the Microfiltration Process

The performance of membrane filtration (including microfiltration) has been characterized in terms of membrane flux and solute removal by numerous researchers (Abadi et al., , Gai and Kim, 2008, Gray et al., 2007, Gray et al., 2008, Howe et al., 2006, Ziegmann et al.). The factors affecting microfiltration performance are briefly discussed in this part, and will be elaborated in the following parts.

#### 2.1.5.1. Flux

The microfiltration membrane flux is governed by an equation similar to Darcy's law as shown in Eq. 2-3. The equation discloses that the flux when filtrating clean water is only determined by the pressure difference between the feed and permeate sides of the



membrane (referred to as transmembrane pressure (TMP)), water viscosity, and the hydraulic resistance of the membrane. Although the TMP and viscosity can be easily determined, the membrane resistance relies on a series of factors such as membrane porosity (both surface and internal) (Elimelech et al., 1997, Fu et al., 2008, Ho and Zydney, 1999a, , 2000a, 2000b, , 2002, Hoek et al., 2003), pore size (Cheryan, 1998, Tarleton and Wakeman, 1994), and membrane material (Capannelli et al., 1990, Fan et al., 2001, Fontyn et al., 1991, Gray et al., 2007).

When fouling occurs during filtration of a solution or suspension, membrane permeate flux can be described by a “resistance-in-series” model as shown in Equation 2-4 (Bouchard et al., 1994, Juang et al., 2008, Yeh and Wu, 1997).

$$J = \frac{\Delta P}{\mu_p(R_m + R_a + R_p + R_c)} \quad \text{Eq. 2-4}$$

Where

$J$  is the flux through the membrane ( $\text{Lh}^{-1}\text{m}^{-2}$ );

$\Delta P$  is the applied pressure (pa);

$\mu_p$  is the viscosity of permeate ( $\text{Pa} \cdot \text{S}$ );

$R_m$  is the hydraulic resistance of membrane ( $\text{m}^{-1}$ );

$R_a$  is the resistance due to solute adsorption ( $\text{m}^{-1}$ );

$R_p$  is the resistance due to concentration polarization;

$R_c$  is the cake resistance ( $\text{m}^{-1}$ ).

At the initial stage of a membrane process, there is no or very little foulant on membrane surface. Solute adsorption inside the membrane accounts for the primary fouling of the membrane. With constant transport of the solute to the membrane surface,

the solutes larger than the pore size are retained on the membrane, and the buildup of the solutes on the membrane surface is called concentration polarization and causes more membrane resistance. The continuous accumulation of foulant on the membrane surface will finally result in a cake layer formed on the membrane surface. According to Equation 2-4, any of the three types of fouling process above will bring extra resistance to the filtration process and reduce the flux through the membrane.

#### **2.1.5.2. Solute Removal**

Contaminant removal occurs due to retention of contaminants by the membrane. The retention of solutes depends on a variety of factors including size and shape of the molecules, membrane properties, operating parameters, lot variations, membrane configuration, and membrane fouling (Munir, 1998). In general, molecules or particles significantly smaller than the membrane pore size will pass through while those larger than the pore size will be retained on the membrane surface. A molecule with an agglomerated conformation is more easily retained by the membrane than a linear molecule; as the conformation of a molecule is usually a function of feed water pH and ionic strength (Yuan et al., 2002, Yuan and Zydney, 1999a, 1999b, , 2000), solution chemistry plays an important role in solute rejection. The mechanisms of solute retention are also different for membranes with different pore size (Schafer et al., 2000a). For MF and UF, the primary mechanism of rejection is size exclusion; Donnan exclusion is an important mechanism for ion rejection in NF and RO. Membrane fouling can affect rejection in all four membrane processes. In MF, pore plugging reduces the pore size, while the cake layer acts as an additional filter, both increasing rejection; in UF, internal pore adsorption reduces the internal pore diameter and subsequently increases rejection.

In NF and RO, the key factor appears to be the charge of the deposit. If the precipitate is positively charged, the rejection of positively charged solutes will increase and that of negatively charged solutes will decrease.

## **2.2. Fouling of Microfiltration Membranes**

### **2.2.1. Foulant of Microfiltration Membrane**

Typical surface water contains natural organic matter (NOM), micro-organism (bacteria, algae, and protozoa such as giardia and cryptosporidium), ions, inorganic colloids (Buffle and Leppard, 1995, Carroll et al., 2000, Schafer et al., 2000a, Schafer et al., 2000b) and so on. Among all the foulants, NOM (including both colloidal and dissolved NOM) microorganism and inorganic matter have been widely investigated for MF. The discussion of the primary foulants is presented in the following sections.

#### **2.2.1.1. Natural Organic Matter**

NOM originates from broken down organic matters from plants and animals in the environment, the basic structures of NOM molecules are largely from cellulose, tannin, and lignin, along with other various proteins, lipids, and sugars (Grathwohl, 1990). NOM exists in the water body in both colloidal and dissolved forms. The portion of aquatic natural organic matter (NOM) that can pass through a 0.45  $\mu\text{m}$  membrane filter is defined as dissolved organic matter (DOM), which is usually quantified as the amount of dissolved organic carbon (DOC). The DOC value is approximately 50% of the amount of DOM according to Kulovaara et al. (1999). In the case of drinking-water microfiltration,

colloidal material may cause fouling by adsorbing inside membrane pores and forming a cake on the membrane surface, while dissolved material may cause fouling by precipitating on the membrane surface through both steric and electrostatic exclusion (Amy and Cho, 1999) or adsorbing within the membrane pore space (Amy and Cho, 1999, Carroll et al., 2000).

#### 2.2.1.1.1. Colloidal NOM

In a microfiltration system, membrane fouling is mainly caused by colloidal material when the raw water was filtered untreated according to Carroll et al. (2000). As stated previously, colloids in surface water include both organic and inorganic forms, both of which have been reported to contribute to membrane fouling (Howe and Clark, 2002). However, organic colloids were identified to cause more membrane fouling than inorganic colloids (Howe and Clark, 2002) and the fouling caused by organic colloids are mostly hydraulically reversible (Huang et al., 2007). Specifically, it was found that small colloids ranging from 3 to 20 nm in diameter are important membrane foulants (Howe and Clark, 2002). The adhesive energies between colloids and between colloids and membrane surface were determinative in membrane colloidal fouling according to Brant et al. (2002), these authors thus concluded that it is necessary to assess the adhesive energy between the membrane and the colloid to predict the fouling behavior instead of the surface energies of a membrane alone. They also recommended focusing on means for minimizing colloid–membrane and colloid–colloid interaction energies during membrane filtration processes instead of focusing attention only on manufacturing “low-energy membranes” and disregarding the interfacial properties of the foulants.

#### 2.2.1.1.2. Dissolved NOM

Dissolved NOM can be fractionated into three groups: hydrophobic (humic substances), hydrophilic, and transphilic fractions (Zularisam et al., 2006). The hydrophobic humic substances contain aromatic NOM compounds (Cho et al., 2000) and are negatively charged due to the dissociation of matters containing carboxyl and hydroxyl functional groups (Schafer et al., 2000b). Humic substances have been reported to account for 50% - 90% of the dissolved NOM depending on the sources (Schafer et al., 2000b, Zularisam et al., 2006). Humic substances are more soluble at high pH, and assume long linear conformations at high pH and low ionic strength because of charge repulsion between functional groups. When the pH is low but ionic strength is high, humic substances will be coiled spherical molecules (Schafer et al., 2000b). The hydrophilic fraction is composed of 25–40% of dissolved organic carbon (DOC) with lower MW (polysaccharides, amino acids, protein, etc.). The transphilic fraction is comprised of approximately 25% DOC in natural water but with MW in between hydrophobic and hydrophilic fractions (Zularisam et al., 2006).

A large number of studies during the last decade have demonstrated that the hydrophilic non charged fraction of NOM (polysaccharide like organic matter) caused the major membrane fouling (Aoustin et al., 2001, Carroll et al., 2000, Cho et al., 1998, Fan et al., 2001, Kimura et al., 2006, Manttari et al., 2000, Yamamura et al., 2008, Yamamura et al., 2007, Zularisam et al., 2007). Fan et al. (2001) identified the following fouling potential of the different NOM fractions: hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. The strong fouling potential of the hydrophilic noncharged fraction of NOM was possibly due to its large amount of hydroxyl groups,

which easily form hydrogen bonds with the functional groups on the membrane surface (Yamamura et al., 2008).

#### **2.2.1.2. Microorganisms and Inorganic Matters**

Besides NOMs, other matters such as microorganisms and inorganic matters, also contribute to the fouling of microfiltration membrane. The fouling caused by microorganisms is sometimes referred to as biofouling. Biofouling can destroy the membrane structural integrity, bring irreversible membrane damage, shorten membrane life, and increase operational and maintenance costs (Hilal et al., 2005). Biofouling of MF membranes has been mainly reported in membrane bioreactors used for wastewater treatment (Kim and Jang, 2006, Ramesh et al., 2007, Ramesh et al., 2006, Sombatsompop et al., 2006). Bacterial microfiltration has also been studied (Chellam and Cogan, 2011, Cogan and Chellam, 2009). In these applications, microorganisms foul the membranes through either the microorganisms themselves or the extracellular polymeric substances secreted by these microorganisms.

Although inorganic matter has not been reported to be a major foulant in microfiltration, inorganic species including Si, Al, Fe, and Mn do contribute to MF fouling (Howe and Clark, 2002, Yamamura et al., 2008). Suspended solids are present at significant concentrations in surface waters, but they seldom create fouling problems for MF system because of their large sizes.

## **2.2.2. Factors Affect Membrane Fouling**

Membrane fouling is a result of interactions between the membrane and various solutes in the feed water. Although it is very difficult to establish general rules about the nature and extent of fouling that will be universally applicable, factors affecting membrane fouling can be generally categorized into two groups: feed water condition (e.g. pH, salt concentration, and divalent cations) and membrane intrinsic characteristics (e.g. membrane material, porosity, and roughness) (Moulder, 2003).

### **2.2.2.1. Effect of Solution Chemistry**

pH is a well known important parameter in membrane filtration. pH influences membrane fouling mainly through alternating the properties of NOM (e.g. charge property, conformation, and aggregation), cake layer (e.g. porosity and tightness), and the membrane (e.g. surface charge). It has been showed by many studies that lower pH led to more membrane fouling (Hong and Elimelech, 1997, Kulovaara et al., 1999, Yuan and Zydney, 1999a). For example, Yuan and Zydney (1999a) showed that fouling of a MF membrane by humic substance was the highest at pH 3 compared to pH 4.7, 7, and 9. Under lower pH, on one hand, the negative charges of both the NOM molecules and the membrane surface could be neutralized leading to more attachment of NOMs onto the membrane surface (thicker cake layer); on the other hand, more inter and intra molecular aggregation of NOM molecules induced by a reduced negative charge of humic substance would bring a denser cake layer (Hong and Elimelech, 1997). However, the study of Yuan and Zydney (1999a) clearly showed that the more membrane fouling at lower pH was caused by a thicker instead of a denser cake layer.

The effect of salt concentration on membrane fouling by NOM is reported to be similar to that of pH (Hong and Elimelech, 1997, Yuan and Zydney, 1999a). Higher salt concentration causes double layer compression and charge screening, thus the electrostatic repulsions between NOM molecules and between NOM molecules and membrane surface can be reduced. The resulting cake layer is then both thicker and denser according to Hong and Elimelech, but only denser and less permeable according to Yuan and Zydney.

Calcium and other multivalent cations are known to interact with NOM molecules through ways such as partially neutralize their surface charge (Schafer et al., 2000b) and form intra- or intermolecular bridges between the negatively charged humic acid molecules (Yuan and Zydney, 1999a). It is agreed that these interactions lead to formation of large aggregates of NOM molecules, and thus more fouling for microfiltration membrane (Schafer et al., 2000b, Yuan and Zydney, 1999a) and ultrafiltration membrane (100 kDa MWCO) (Aoustin et al., 2001). The reason is probably that microfiltration and ultrafiltration membranes have larger membrane pores than nanofiltration membrane. The NOM aggregates induced by calcium are able to adsorb onto the pore wall of microfiltration and ultrafiltration membranes causing constriction and closure of the pores. In addition, calcium has been found to increase irreversible membrane fouling (Aoustin et al., 2001, Schafer et al., 1998).



#### **2.2.2.2. Effect of Membrane Properties**

Membrane properties that can significantly affect its fouling behavior include membrane hydrophilicity and surface charge, surface morphology, surface modification, and so on. (Munir, 1998).

The importance of membrane surface hydrophobicity in membrane fouling by organic matter has long been recognized (Capannelli et al., 1990, Fan et al., 2001, Fontyn et al., 1991, Gekas et al., 1992, Gray et al., 2007, Jonsson and Jonsson, 1995). Hydrophobicity/hydrophilicity is usually characterized through contact angle measurement. A larger contact angle between liquid and solid surface (e.g. water and membrane surface) indicates the solid material is more hydrophobic (As discussed in previous part, PVDF and PTFE are usually hydrophobic and the cellulose family is usually hydrophilic). In the research of the above authors, it was generally identified that the membrane flux reduced significantly with hydrophobic membranes compared to hydrophilic membranes. Since a majority of the organic matter in surface water is hydrophobic (Schafer et al., 2000b, Zularisam et al., 2006), if the membrane material is hydrophobic, the hydrophobic organic matter will adsorb more easily onto the membrane and result in faster membrane fouling. However, a few recent studies suggested that membrane hydrophobicity is not a reasonable predictor of organic foulant adsorption (Combe et al., 1999, Contreras et al., 2011, Li et al., 2007). Contreras et al. actually demonstrated that specific interactions between individual chemical functional groups were much more important. They suggested that hydrophilicity is not an appropriate parameter for estimating fouling potential. The conclusion of Contreras et al. supported the research of Brant et al. (2002), which concluded that interaction energies between

colloids and between colloids and membrane surface were much more important than the membrane surface energy alone.

Most membranes have a negative charge under usual process conditions (Munir, 1998). Therefore, membrane surface charge becomes very important when charged materials are processed. Electrostatic interaction is then a primary interaction between a charged membrane surface and charged solutes. Normally, for a negatively charged membrane, an increase in the charge density on membrane surface will increase solute rejection and reduce membrane fouling (Han et al., 2011).

Membrane morphology is another important factor that can affect membrane fouling. Morphology was normally referred to as characteristics such as membrane surface roughness, porosity, pore size, and inside interconnectivity. For the membranes with similar water permeability, lower surface porosity was found to result in more membrane fouling (Fu et al., 2008, van der Marel et al., 2010). Possibly, the low surface porosity membranes lead to almost immediate external fouling, but the higher surface porosity membranes allow for a significant period of time for internal fouling to occur (Mueller and Davis, 1996).

Regarding the membrane surface roughness, smoother membranes have been identified to have less fouling potential for high pressure membranes (reverse osmosis and nanofiltration) (Elimelech et al., 1997, Hoek et al., 2003, Lee et al., 2005a, Vrijenhoek et al., 2001, Wei et al., 2009). However, the effect of membrane surface roughness on membrane fouling is inconclusive for low pressure membranes. On one hand, surface roughness was reported by some researchers to be the dominant factor in

membrane fouling, and higher membrane surface roughness leads to higher membrane biofouling (Kochkodan et al., 2006, Tsuyuhara et al., 2010); On the other hand, some others showed that membrane fouling was lower with increase membrane surface roughness (Kang et al., 2001, Peng et al., 2004). But a common phenomenon observed for both low and high pressure membranes is that foulant materials tend to deposit in the valleys of the rough membrane (Hoek et al., 2003, Lee et al., 2005a, Riedl et al., 1998, Vrijenhoek et al., 2001).

Many studies have shown that membrane (especially microfiltration membrane) with larger pores will firstly have higher flux than tighter membranes but will eventually have lower flux as indicated in Figure 2-5 (a) (Tarleton and Wakeman, 1994). A possible reason has been elaborated by Cheryan (1998). Basically, the big pores of a looser membrane (membrane with larger pores) usually afford a majority part of the flux through the membrane. For example, if the pore distribution is 0.1  $\mu\text{m}$  pores (10%), 0.2  $\mu\text{m}$  pores (80%), 0.5  $\mu\text{m}$  pores (10%), 43% of the water permeation will occur through the 0.5  $\mu\text{m}$  pores. When the membrane pores are larger than the particles to be separated, the big pores tend to be plugged first during the filtration, which will cause a rapid flux drop in the first few minutes of operation. On the contrary, when the membrane pores are much smaller than the particle size, the particles will not get caught within the pores. In addition, Cheryan (1998) stated that an inverse parabolic relationship between average flux and pore size exists as shown in Figure 2-5 (b). For a feed that has a certain size distribution of particles, membrane of both too large pores and too small pores will lead to reduced average flux.

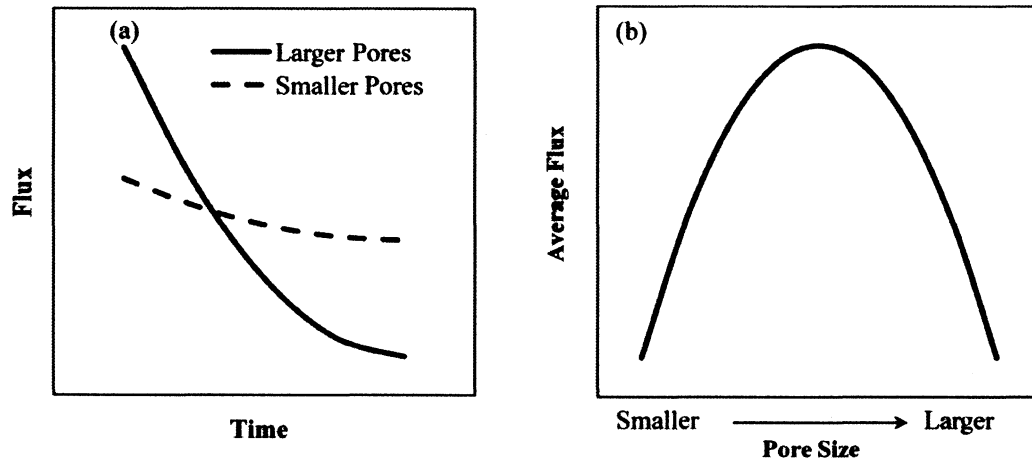


Figure 2-5 Effect of membrane pore size on flux: (a), instantaneous flux versus time, all other conditions were the same; (b), average flux over an operating cycle (e.g. between cleanings) versus pore size, all other conditions were the same.

The relation between membrane flux and interconnectivity of microfiltration membranes has been illustrated in details by Ho and Zydney (Ho and Zydney, 1999a, 1999b, , 2000b, Zydney and Ho, 2003). Their main conclusion is that membranes with highly interconnected pores show much slower rates of flux decline than straight-through membranes, because the disturbance generated by surface fouling penetrates only a small distance into the membrane and the fluid could flow around the blocked pores through the interconnected pore structure.

### 2.2.2.3. Membrane Modification

The purposes of membrane surface modifications are generally making membranes less prone to fouling, longer membrane life time, and higher contaminant rejection (Carroll et al., 2002, Mueller and Davis, 1996, Rana et al., 2005, Taniguchi et

al., 2003). Commonly used surface modification methods include surface coating and grafting of hydrophilic groups. For example, grafting with hydrophilic monomers onto UF membrane was reported to increase membrane surface wettability and shift the membrane pore size distribution to smaller sizes, which increased natural organic matter rejection (Taniguchi et al., 2003). Carroll et al. (2002) reported that a membrane graft-modified with hydrophilic matter had a 50% lower membrane fouling than unmodified membrane.

#### **2.2.2.4. Synergistic Effect**

NOM fouling can be much worse when other foulants exist in the system. For example, a significant synergistic effect was observed by Li et al. (2006) in their study of a nanofiltration system containing both colloids and organic matter. The flux decline rate was significantly higher than the sum of colloidal and organic fouling alone. Similar effect has been observed in studies on ultrafiltration membranes (Guo et al., 2009, Jermann et al., 2008a, Jermann et al., 2008b, Jermann et al., 2007).

### **2.2.3. MF Membrane Fouling Mechanisms**

Because only constant flux, dead end mode microfiltration was adopted in this research, the following discussion on fouling mechanisms is based on constant flux -, dead end filtration.

### 2.2.3.1. Development History of Fouling Mechanism Model

Most of the current fouling mechanism models assume uniform pore size and non-stirring condition. The earliest dead end filtration fouling mechanism was developed by Hermans and Bredee (1935) under constant pressure dead end filtration mode. Their models included: (1) complete blocking law, which assumes each particle entering the membrane completely clogs one pore on the surface; (2) standard blocking law, which assumes small particles form an internal deposit on the pore walls; (3) Intermediate law, which was introduced empirically to compromise the complete and standard blocking laws. In 1950, Gonsalves (1950) made a critical study of their physical meaning. Six years later, Grace (1956) proposed the concept of applying different laws for different parts of the curve of filtrate volume versus time. By 1982, a mathematic elucidation of the intermediate law was developed by Hermia et al. (1982) together with the equations for non-newtonian fluids. In 1993, Hlavacek et al. (1993) developed their blocking laws based on constant flow rate filtration. After that, Zydney of the Pennsylvania State University and his students did a vast amount of work on combined fouling mechanisms, and some models incorporated the membrane surface morphology (Duclos-Orsello et al., 2006, Ho and Zydney, 1999a, 1999b, , 2000a, , 2002, Kelly and Zydney, 1994, Yuan et al., 2002, Zydney and Ho, 2003). Glen Bolton from Millipore also made a significant contribution to the development of combined fouling mechanisms (Bolton et al., 2006a, Bolton et al., 2006b).

### 2.2.3.2. Basic Fouling Mechanisms

Modern microfiltration membrane fouling models were all based on the four classical blocking law models developed by Hermia et al. (1982). The fundamental ideas of the Hermia blocking laws are shown in Figure 2-6: (a) Standard blocking, also referred to as the “pore constriction” mechanism, assumes that foulants smaller than the membrane pores attach to the pore wall and restrict the permeate flow; (b) Complete blocking, which assumes that the foulant molecule/particle blocks the membrane pore completely, and there is no flux of either the solvent (e.g., water) or the solute (e.g., the foulant) through the blocked pores; (c) Intermediate blocking assumes that the membrane pore is blocked by the foulant, but the blocked pore still allows the solvent to go through at a lower rate; (d) Cake filtration describes the increase in hydraulic resistance due to the cake layer resulting from accumulation of foulants on the membrane surface.

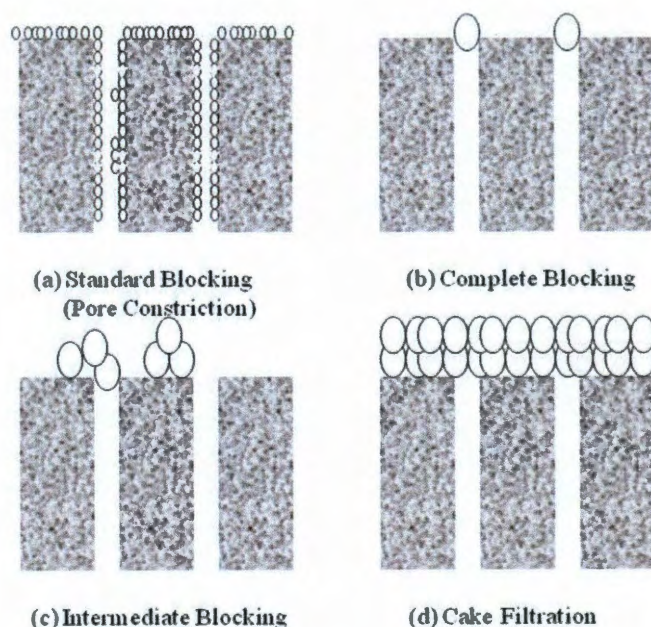


Figure 2-6 Basic fouling mechanisms

### 2.2.3.3. Basic Blocking Laws

Because constant flow rate filtration and constant flow rate blocking laws were employed in this research, the mathematical models for the first three mechanisms developed by Havacek et al. (1993) under constant flow rate condition are introduced as follows.

The constant flow rate blocking laws are based on the following assumptions:

The membrane pores are parallel and straight with a radius of  $r$  and a length of  $L$ ;

The flow regime is laminar;

The filtrate flow rate  $Q$  is constant and equal to the ratio of the volume of filtrate  $V$  to the time  $t$  ( $Q = V/t$ ).

All the particles entering the membrane unit are captured;

Because the model is based on pore plugging mechanisms, the relevant area in the mathematical development is not the membrane area  $A$ , but it is the pore area  $S$ . The initial total pore area  $S_0$ , is related to the membrane area by the porosity  $\varepsilon$  ( $S_0 = \varepsilon A$ ).

#### Complete Blocking Law

In the complete blocking law, each particle coming into contact with the membrane plugs perfectly one pore. No superimposition of particles is possible. Consequently, the reduction of the active surface is proportional to the volume of filtrate:

$$S = \varepsilon A - \sigma V \quad \text{Eq. 2-5}$$

Where  $S$  is free pore area,  $\text{m}^2$ ;



$\varepsilon$  is membrane surface porosity;

$A$  is membrane surface area,  $\text{m}^2$ ;

$\sigma$  is clogging coefficient and is a characteristic of the suspension;

$V$  is the filtrate volume,  $\text{m}^3$ .

The pressure drop is given by a modified Darcy's law

$$\Delta P = \frac{R_m \mu Q}{S} \quad \text{Eq. 2-6}$$

Where  $\Delta P$  = transmembrane pressure, Pa;

$R_m$  = membrane resistance,  $\text{m}^{-1}$ ;

$\mu$  = viscosity of water,  $\text{Pa} \cdot \text{s}$ ;

$Q$  = flow rate,  $\text{m}^3/\text{S}$ .

Combining Eq. 2-5 and 2-6 yields

$$\frac{1}{\Delta P} = \frac{1}{\Delta P_0} - \frac{\sigma V}{R_m \mu Q} \quad \text{Eq. 2-7}$$

in which

$$\Delta P_0 = \frac{R_m \mu Q}{\varepsilon A}$$

where  $\Delta P_0$  = initial transmembrane pressure, Pa;

### Standard Blocking Law

In the standard blocking law, the increase of the hydraulic resistance is the result of uniform particle deposition inside the pores. During a time interval  $dt$ , the volume of filtered suspension is  $dV=Q dt$ . The reduction of the free volume of  $N$  pores (i.e. the initial pore volume less the volume of deposited particles) is expressed by:

$$-N(2\pi r dr)L = cdV \quad \text{Eq. 2-8}$$

where  $c$  is the volume of deposit per unit volume of filtered suspension.

Integration of Eq. 2-8 leads to:

$$r^2 = r_0^2 - \frac{cV}{\pi NL} \quad \text{Eq. 2-9}$$

The Hagen-Poiseuille law relates the flow  $Q$  to the pore radius

$$Q = N \frac{\pi r^4 \Delta P}{8\mu L} \quad \text{Eq. 2-10}$$

Combining Eq. 2-9 and 2-10 gives the expression for the standard blocking law:

$$\frac{1}{\sqrt{\Delta P}} = \frac{1}{\sqrt{\Delta P_0}} - \frac{cV}{\sqrt{8\pi N\mu L^3 Q}} \quad \text{Eq. 2-11}$$

### Intermediate Blocking Law

In the case of intermediate blocking law, particles can deposit on any part of the membrane surface, and thus superimposition of particles is possible. In addition, a pore is plugged completely when a particle deposit on it. The decrease of free surface  $dS$  is proportional to the free surface  $S$ . This reduction of the free surface of pores is identical to the probability for a pore to get blocked:

$$\frac{dS}{dV} = -\sigma \frac{S}{\epsilon A} \quad \text{Eq. 2-12}$$

By integrating Eq. 2-12, the following equation can be obtained:

$$S = \epsilon A \exp\left(\frac{-\sigma V}{\epsilon A}\right) \quad \text{Eq. 2-13}$$

Using Darcy's Law (Eq. 2-3), we obtain:

$$\Delta P = \Delta P_0 \exp\left(\frac{\sigma V}{\epsilon A}\right) \quad \text{Eq. 2-14}$$

Experimental curves can be tested with the linearized equations, which are summarized in Table 2-3 together with the original mathematical expressions.

Table 2-3 Mathematical expression of the blocking laws

Blocking Law	Governing equation	Linearized form
Complete	$\frac{1}{\Delta P} = \frac{1}{\Delta P_0} - \frac{\sigma V}{R_m u Q}$	$\frac{1}{\Delta P} = a + b V$
Standard	$\frac{1}{\sqrt{\Delta P}} = \frac{1}{\sqrt{\Delta P_0}} - \frac{c V}{\sqrt{8\pi N u L^3 Q}}$	$\frac{1}{\sqrt{\Delta P}} = a' + b' V$
Intermediate	$\Delta P = \Delta P_0 \exp \frac{\sigma V}{\epsilon A}$	$\ln(\Delta P) = a'' + b'' V$

#### 2.2.3.4. Models Combining Pore Blockage and Cake Filtration

Ho et al. (2002) developed an advanced constant flux blocking model to describe a combined fouling of pore blockage and cake filtration based on a track-etched membrane. The model used three fitted parameters and an approximate solution was also

provided to allow calculation of flux as a function of time without integrating. Plots of pressure versus time during constant flow operation were obtained by numerical integration of the relevant equations. The values of the fitted parameters were similar to the values obtained by independent experiments. The authors found this model provided good data fits and made accurate membrane sizing estimates for the fouling of microporous track-etched membranes by five proteins. The main assumptions for this model are listed below:

- (1) this initial deposit is at least partially permeable to fluid flow, i.e. there is a small flow through even the “blocked” pores;
- (2) Cake growth occurs simultaneously with the coverage (or blockage) of the remaining open area of the membrane;
- (3) The resistance of the protein layer is uniform across the fouled region of the membrane, neglecting the variation in the thickness of this layer associated with the different time at which each region was first fouled.

The transmembrane pressure drop across the fouled membrane can be expressed in terms of the flow rates through the open ( $Q_{open}$ ) or blocked pores ( $Q_{blocked}$ ) as shown in Eq. 2-15 and 2-16.

$$\Delta P = \frac{Q_{open} \mu R_m}{A_{open}} \quad \text{Eq.2-15}$$

$$\Delta P = \frac{Q_{blocked} \mu (R_m + R_p)}{A_{blocked}} \quad \text{Eq.2-16}$$

Where  $\mu$  = solution viscosity;

$A_{open}$  = the areas of the open regions of the membrane at time  $t$ ;

$A_{blocked}$  = the areas of the blocked regions of the membrane at time  $t$ ;

$R_m$  = the resistance of the clean membrane;

$R_p$  = the resistance of the protein deposit;

The total flow rate through the partially fouled membrane ( $Q_0$ )

$$Q_0 = Q_{open} + Q_{blocked} \quad \text{Eq.2-17}$$

The total flow rate remains constant during the constant flux filtration.

Combining Eq. 2-15 to 2-17, the transmembrane pressure can be expressed as a function of the open pore area and the pore area and the protein layer resistance as shown in Eq. 2-18

$$\Delta P = \mu Q_0 R_m \frac{R_m + R_p}{A_0 R_m + A_{open} R_p} \quad \text{Eq.2-18}$$

Where  $A_0 = A_{open} + A_{blocked}$

The rate of pore blockage is assumed to be proportional to the convective flow rate of protein aggregates to the open regions of the membrane surface:

$$\frac{d(\varepsilon A_{open})}{dt} = -\alpha Q_{open} C_b \quad \text{Eq.2-19}$$

Where  $C_b$  = the bulk protein concentration

$\varepsilon$  = the membrane porosity

$\alpha$  = is a pore blockage parameter and is equal to the fraction of the total membrane pore area blocked per unit mass of protein convected to the membrane surface.

For the low porosity polycarbonate membrane used in this study, Ho et al. expected that a given protein aggregate is able to block only a single pore. Under these conditions:

$$\alpha = \frac{fA_{\text{pore}}}{M_{\text{agg}}} \quad \text{Eq.2-20}$$

Where  $f$  = fractional amount of protein present in the bulk solution as Large aggregates;  $f$  can also account for the reduction in protein deposition due to any back-flux phenomena, including the effects of crossflow and any long-range electrostatic interactions.

$A_{\text{pore}}$  = the area of a single pore;

$M_{\text{agg}}$  = the mass of a single aggregate.

The total protein layer resistance is assumed to be proportional to the mass of the protein deposit per unit cross-sectional area( $m_p$ ):

$$R_p = R' m_p + R_{p0} \quad \text{Eq.2-21}$$

Where  $R'$  = specific cake resistance, which is a function of the transmembrane pressure due to the compressibility of the protein deposit;

$R_{p0}$  = resistance of the initial protein aggregate that deposits on the membrane.

$A_{\text{pore}}$  = the area of a single pore;

$M_{\text{agg}}$  = the mass of a single aggregate.

The specific cake resistance can be expressed using a power law relationship

$$R' = k_p \left( \frac{\Delta P}{1 \text{ N m}^{-2}} \right)^S \quad \text{Eq.2-22}$$

Where

$S$  = the compressibility parameter, which varies from 0 for an incompressible cake to 1 for a very highly compressible cake;

$R_{p0}$  = resistance of the initial protein aggregate that deposits on the membrane.

$A_{\text{pore}}$  = the area of a single pore;

$M_{\text{agg}}$  = the mass of a single aggregate.

The growth of the protein deposit is assumed to be proportional to the convective transport of protein the blocked regions of the membrane

$$\frac{dm_p}{dt} = \frac{f' Q_{\text{blocked}} C_b}{A_{\text{blocked}}} \quad \text{Eq.2-23}$$

Where

$f'$  = the fraction of the protein that contributes to the growth of the deposit.  $f'$  will be equal to  $f$  under conditions where only the protein aggregates add to the growing deposit.

Eqs 2-19 and 2-23 can be solved numerically using Euler integration with the protein layer resistance at each time step evaluated from Eqs. 2-21 and 2-22 using the transmembrane pressure from the previous time step ( $t-\Delta t$ ).

An approximate solution for the pressure drop was developed by Ho et al. Combining Eq. 2-15 and 2-18, Eq. 2-24 can be obtained

$$\frac{d(\varepsilon A_{\text{open}})}{dt} = -\alpha Q_0 C_b \frac{A_{\text{open}}(R_m + R_p)}{A_0 R_m + A_{\text{open}} R_p} \quad \text{Eq.2-24}$$

Eq. 2-24 can be separated and integrated by assuming that  $R_p \approx R_{p0}$ , i.e. the protein layer resistance remains at its initial value as the membrane pores become blocked. This approximation will be valid when the rate of cake growth is slow relative to the rate of aggregate deposition. Under these conditions, the following implicit equation was obtained for  $A_{open}$  as a function of time:

$$\frac{A_0 R_m}{R_m + R_{p0}} \ln \left( \frac{A_{open}}{A_0} \right) + \frac{R_{p0}}{R_m + R_{p0}} (A_{open} - A_0) = \frac{\alpha}{\varepsilon} Q_0 C_b t \quad \text{Eq.2-25}$$

The rate of cake growth Eq. 2-23 can be rewritten as a differential expression in terms of the open pore area using Eq. 2-19, with  $Q_{open}$  evaluated from Eqs. 2-15 and 2-18 to give

$$dm_p = -\left(\frac{\varepsilon f'}{\alpha}\right) \frac{R_m}{R_m + R_p} \frac{dA_{open}}{A_{open}} \quad \text{Eq.2-26}$$

Eq. 2-26 can also be integrated analytically assuming that  $R_p \approx R_{p0}$  to give:

$$m_p = -\left(\frac{\varepsilon f'}{\alpha}\right) \frac{R_m}{(R_m + R_{p0})} \ln \left( \frac{A_{open}}{A_0} \right) \quad \text{Eq.2-27}$$

### 2.2.3.5. Models Combining Different Fouling Mechanisms

Bolton et al. (2006a) expanded the combined constant flux blocking model to account for combined effects of different individual fouling mechanisms derived from Darcy's law. Explicit equations were derived to relate pressure to time during constant flow operation. All of these models employed two fitted parameters and can be reduced to individual models in the absence of the second fouling mechanisms. The equations for five combined fouling are listed in Table 2-4.



Table 2-4 Models combining different fouling mechanisms

Model	Equation	Fitted parameters
Cake-Complete blocking	$\frac{P}{P_0} = \frac{1}{(1 - K_b t)} \left( 1 - \frac{K_c J_0^2 t}{K_b} \ln(1 - K_b t) \right)$	$K_c \text{ (s/m}^2\text{)}, K_b \text{ (s}^{-1}\text{)}$
Cake-Intermediate blocking	$\frac{P}{P_0} = \exp(K_i J_0 t) \left( 1 + \frac{K_c J_0}{K_i} (\exp(K_i J_0 t) - 1) \right)$	$K_c \text{ (s/m}^2\text{)}, K_i \text{ (m}^{-1}\text{)}$
Complete-Standard blocking	$\frac{P}{P_0} = \frac{1}{(1 - K_b t) \left( 1 + \frac{K_s J_0}{2 K_b} \ln(1 - K_b t) \right)^2}$	$K_b \text{ (s}^{-1}\text{)}, K_s \text{ (m}^{-1}\text{)}$
Intermediate-Standard blocking	$\frac{P}{P_0} = \frac{\exp(K_i J_0 t)}{\left( 1 - \frac{K_s}{2 K_i} (\exp(K_i J_0 t) - 1) \right)^2}$	$K_i \text{ (m}^{-1}\text{)}, K_s \text{ (m}^{-1}\text{)}$
Cake-Standard blocking	$\frac{P}{P_0} = \left( 1 - \frac{K_s J_0 t}{2} \right)^{-2} + K_c J_0^2 t$	$K_c \text{ (s/m}^2\text{)}, K_s \text{ (m}^{-1}\text{)}$

Note:  $J_0$  = initial flux (m/s),  $K_b$  = complete blocking constant ( $\text{s}^{-1}$ ),  $K_c$  = cake filtration constant ( $\text{s/m}^2$ ),  $K_i$  = intermediate blocking constant ( $\text{m}^{-1}$ ),  $K_s$  = standard blocking constant ( $\text{m}^{-1}$ ),  $P$  = transmembrane pressure at time  $t$  ( $\text{kg/ms}^2$ ),  $P_0$  = initial transmembrane pressure ( $\text{kg/ms}^2$ )

#### 2.2.4. Fouling Control Strategies

Because the membrane process alone is not able to remove sufficient natural organic matter and the membrane is susceptible to fouling, it is necessary to take measures to enhance the NOM removal to prevent potential formation of disinfection byproducts (DBPs) and to mitigate membrane fouling.

#### 2.2.4.1. General Strategies

Several strategies can be adopted to control membrane fouling including: membrane materials/surface modification, optimization of operating parameters, membrane cleaning, and pretreatment of feed water (Hilal et al., 2005).

As discussed previously, membrane modification is widely used to minimize membrane fouling by changing membrane properties such as surface wettability and membrane pore size distribution (Taniguchi et al., 2003). Many flow manipulation methods such as using inserts mixers or turbulence promoters, increasing flow rate to provide higher shear, back flushing, pulsing, air sparging, can be used to reduce membrane fouling. These measures are used to increase permeate flux by reducing the adverse effects of concentration polarization and membrane fouling (Hilal et al., 2005).

Hydraulic and chemical cleaning are effective methods widely used in practice to remove membrane foulants and recover membrane flux. Reagents that can be used for chemical cleaning include sodium hydroxide, oxidants (e.g. hydrogen peroxide and sodium hypochlorite), acids (e.g. hydrochloric acid, sulphuric acid, citric acid, and oxalic acid), and additives such as EDTA (ethylenediamine tetraacetic acid) (Porcelli and Judd, 2010). Sodium hydroxide can dissolve the weakly acidic organic matter (e.g. organic matter with carboxyl and phenolic functional groups), help cleave the polysaccharides and proteins into smaller sugars and amides, and expand NOM molecules allowing effective transport of cleaning reagent to the membrane surface. Oxidation degrades the NOM functional groups to carboxyl, ketonic and aldehyde groups, which make them more susceptible to hydrolysis at high pH levels. This is also the reason that the

combination of oxidants and alkaline cleaning agents are effective in cleaning membrane foulant especially when organic foulants dominate. Acid cleaning aims at removing minerals of multivalent cationic species such as hardness salts. Commonly used cleaning are cleaning-in-place (CIP) and cleaning-out-of-place (COP). CIP takes less time than COP, and thus preferred by industry.

Common feed pretreatment technologies can be divided into four categories: (1) coagulation using various hydrolyzed metal salts (Berube et al., 2002, Fiksdal and Leiknes, 2006, Han et al., 2002, Kim et al., 2006, Kothari and Taylor, 1998, Mo et al., 2002, Moon et al., 2009, Oh and Lee, 2005); (2) adsorption using adsorbent such as powdered activated carbon (Berube et al., 2002, Gai and Kim, 2008, Khan et al., 2009, Lebeau et al., 1998, Mavrov et al., 1998, Zhang et al., 2003); (3) oxidation using for instance ozone (Karnik et al., 2005a, 2005b) and  $\text{TiO}_2$  (Huang et al., 2008); and (4) prefiltration using for instance granular media (Sakol and Konieczny, 2004). The pretreatment for low pressure membranes in water treatment has been well reviewed by several researchers (Farahbakhsh et al., 2004, Huang et al., 2009), who concluded that coagulation is the most effective pretreatment for low pressure membrane filtration.

Coagulation pretreatment is known to increase the solute removal (e.g. particular matter and dissolved NOM) through combining or aggregating the solutes into porous flocs. Coagulation can also reduce microfiltration membrane fouling by preventing pore blockage and possibly increasing the cake permeability (Carroll et al., 2000, Huang et al., 2009, Mo et al., 2002). Two series of coagulant are normally used in surface water treatment: aluminum and iron salts, because of their effectiveness as coagulant, ready availability, and relatively low cost (Bratby, 2006). Common aluminum coagulants

include aluminum sulfate, aluminum chloride, sodium aluminate, aluminum chlorohydrate, polyaluminum chloride, sodium aluminate and so on. Iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride, polyferric sulfate and so on. Because of the excellent stability of polyaluminum chloride (PACl) under various conditions as discussed below, PACl was selected as the primary coagulant in this research.

#### **2.2.4.2. Polyaluminum Chloride (PACl) as Coagulant**

PACl is a polymerized aluminum coagulant emerged in recent decades. Compared to conventional coagulant such as alum, PACl works faster and more efficiently in removing turbidity (Matsui et al. 1998), even though its efficiency on dissolved organic matter is still ambiguous. The prehydrolyzed PACl mainly contains three species according to their reaction with Ferron reagent at different time: monomeric aluminum species  $Al_a$  (1 min after dosing), medium hydrolyzed species  $Al_b$  (2 h after dosing), and colloidal species  $Al_c$  (the rest Al).  $Al_b$  contains primarily  $Al_{13}$  ( $Al_{13}O_4(OH)_{24}^{7+}$ ) and  $Al_c$  refers to colloidal  $Al(OH)_3$ . The content of these species varies drastically depending on conditions such as PACl basicity (value of  $OH/Al$ ), pH, and aging time. Wang et al. (2004) proved that dilution and ionic strength had little effect on the speciation distribution of PACls after dosing; pH and aging time have significant influence when basicity is low. For low basicity PACl, the content of  $Al_a$  is the largest whereas the content of  $Al_b$  and  $Al_c$  is the lowest when pH is below  $\sim 4.5$ . At pH between 4.5 and 8.0, the  $Al_a$  is transformed into large amount of  $Al_b$  and small amount of  $Al_c$  in situ. The percentage of in situ formed  $Al_b$  is usually larger than the preformed  $Al_b$ . When pH is higher than 8.0, the in situ formed  $Al_b$  and  $Al_c$  are largely transformed back to  $Al_a$ .

Recently, It was observed that  $Al_{13}$  molecules can form aggregates at high dosage under alkaline pH condition; a single coiled  $Al_{13}$  aggregate ranges from 300 to 400 nm in length and 2-3 nm in height. These aggregates can further form even larger linear aggregates (Lin et al., 2008a). Bottero et al. (1987) elaborated the change of  $Al_{13}$  species along with basicity.  $Al_{13}$  is stable in solution when basicity  $< 2.3$ . When basicity is between 2.3 and 2.6,  $Al_{13}$  units can form linear aggregates by removing Cl anions from their hydration shells. During this process, the octahedral Al was polymerized and the content of tetrahedral aluminum decreased slowly with time. For  $2.6 < \text{basicity} < 3$ , highly polymerized octahedral layers was generated faster and tetrahedral aluminum disappeared. When basicity equals to 3, the short range order characteristic of bayerite was obtained within 24 hours. Therefore, Bottero et al. (1987) concluded that crystalline Al trihydroxides were formed by solid state structural rearrangement without redissolution steps instead of condensation of flat hexamers made from Al octahedral.

Contaminant removal by  $Al_a$ ,  $Al_b$  and  $Al_c$  species is considered to be through complexation, neutralization and adsorption, respectively, and  $Al_b$  is proposed to be the main factor affecting turbidity and NOM removal (Yan et al., 2008a). It was also proposed that coagulation mechanisms of  $Al_{13}$  and its aggregate are electrostatic patch and inter particle bridging (Matsui et al., 1998, Wu et al., 2007). At neutral and basic pH values, PACl with higher basicity and consequently more stable preformed  $Al_b$  are more efficient for turbidity and NOM removal. At slightly acidic pH, PACl with lower basicity are more efficient since more  $Al_b$  can be formed in situ (Yan et al., 2008b).  $Al_{13}$  or its oligomer binds selectively to carboxylic groups at pH 6 and to phenolic moieties at pH 8 at low Al concentration. At higher coagulant concentrations, the remaining functional

groups also interact with hydrolyzed aluminum (Kazpard et al., 2006). When coagulating humic acid, reformation of long humic acid molecules around the preformed Al species might be induced by the strong association between the humic acid and preformed Al species due to their relatively larger size and higher positive charge (Shi et al., 2007).

Al<sub>13</sub> with a protonated bridging OH group was postulated as the precursor for the decomposition reaction (Furrer et al., 1999). The half-life of Al<sub>13</sub> was found to be from 350 to 43,000 s between pH 2.06 and 3.50, but several hundred hours at pH 5. Besides proton, organic acids such as oxalate, malonate, salicylate, phthalate and benzoate can also lead to decomposition of Al<sub>13</sub> (Amirbahman et al., 2000). Ligands that can form bidentate complexes with “surface” octahedral Al(III) centers are able to decompose Al<sub>13</sub>. The decomposition rates increased with increasing proton and ligand concentrations in the pH range of 2.0 - 4.8. Maison et al. (Masion et al., 1994) included acetate, oxalate, lactate, and salicylate in their study of depolymerization of pure Al<sub>13</sub>. They proposed that the tridecamer is first depolymerized into oligomers, and then into monomers. The decomposition of Al<sub>13</sub> by NOM or humic substances was also observed (Shi et al., 2007, Yan et al., 2008a).

#### **2.2.4.3. Mechanism of NOM Removal by Coagulation**

Generally, coagulant requirement for NOM coagulation is determined by dissolved organic carbon (DOC) concentration (O'Melia et al., 1999), but it has been reported that the removal of humic substances (HS) can be much more than that of DOC (Pikkarainen and Judd, 2005). Three mechanisms exist for HS removal (Lee et al., 2003a,

Yan et al., 2008a): (1) charge neutralization (Bell-Ajy et al., 2000), (2) complexation between functional groups of HS and Al ions or surface hydroxyl on aluminum hydroxide (Davis, 1982, Gregor et al., 1997, Kummert and Stumm, 1980), (3) adsorption (Dempsey, 1989, Semmens and Field, 1980). The adsorption of HS to aluminum hydroxide occurs through surface complexation or ligand exchange (Hundt and Omelia, 1988). Kinetically, HS adsorption happens within several minutes, and the adsorption onto hydrophilic surface is faster than onto hydrophobic surface (Avena and Koopal, 1999). Cho et al. (2006) observed that  $UV_{254}$  absorbance removals were similar regardless of the mixing mode and flocculation time, and the removal of organics was determined at early stage of the flocculation process.

Cationic polymers (e.g. polydiallyldimethylammonium chloride) are sometimes used as primary coagulant in water treatment. Charge neutralization mechanism has been proposed for HS removal (Lee et al., 2003a); polymer charge density was suggested to be the only controlling factor which can affect the removal rate (Kam and Gregory, 2001).

### **2.3. Factors Affecting Membrane Fouling in Coagulation-Microfiltration**

As stated previously, coagulation improves the performance of microfiltration through combining the fine particles and dissolved NOMs into flocs (Mo et al., 2002). It has been suggested by Carroll et al. (2000) that fouling after coagulation pretreatment can be attributed to formed flocs when coagulated water is directly sent to microfiltration

(direct filtration) and to the residual dissolved NOM when coagulation is followed by sedimentation.

### **2.3.1. Coagulation with Sedimentation**

Since most of the colloids and part of the dissolved NOM can be removed through successful coagulation and sedimentation, the properties of the residual dissolved NOM and the properties of the membrane are the key factors that can affect membrane performance. Researchers have shown that the hydrophobic portion of NOM is easier to be removed by coagulation using hydrolyzing metal salts (Sharp et al., 2006a), because the hydrophobic fraction of NOM (including humic and fulvic acids) is an order of magnitude higher in charge density than the hydrophilic fraction (Sharp et al., 2004). Chow et al. (1999) also found that hydrophilic low molecular weight organic matter like proteins, polyhydroxyaromatics and polysaccharides existed after alum treatment. From the perspective of membrane filtration, small, neutral and hydrophilic fraction of NOM has been proposed to contribute the most to microfiltration membrane fouling after coagulation (Carroll et al., 2000, Fan et al., 2001). Kim et al. (2006) further indicated that organic matter such as aliphatic amide, alcoholic compounds, and polysaccharides whose molecular weights range 300-2000 and 20,000-40,000 Da were mainly responsible for the fouling.

The effect of membrane properties on membrane fouling was elaborated in previous section.



### 2.3.2. Direct Filtration

In direct filtration, floc properties (size and fractal dimension) are key factors affecting microfiltration membrane fouling in a coagulation-microfiltration system. The change of floc size and fractal dimension with experimental conditions will subsequently change the specific cake resistance. The fractal dimension is described in detail below.

#### 2.3.2.1. Fractal Dimension

Many structures have been described as fractal objects, and fractal dimension ( $D_f$ ) is widely used to describe structure of aggregates . Some features of fractal structure generalized by Jarvis et al. (2008b) were presented below:

(1), Fractal structure always shows self similarity irrespective of the scale of investigation.

(2), Fractal structure always shows a power law relationship between two variables. The variable couple could be perimeter (P) and length (L), the area (A) and L, or the volume (V) or mass (M) and L.

$$P \propto L^{D_{FP}} \quad D_{FP} \text{ is the perimeter fractal dimension} \quad \text{Eq. 2-28}$$

$$A \propto L^{D_{FA}} \quad D_{FA} \text{ is the area fractal dimension} \quad \text{Eq. 2-29}$$

$$V \text{ or } M \propto L^{D_{FV}} \quad D_{FV} \text{ is the volumetric fractal dimension} \quad \text{Eq. 2-30}$$

(3), May be characterized by a non-integer fractal dimension.

The fractal dimension takes values between 1 and 3, and fractal structures corresponding to various fractal dimensions are illustrated in Figure 2-7. A straight line

has a fractal dimension of 1 while a solid sphere has a fractal dimension of 3. For porous structure, the fractal dimension is located between 1 and 3.

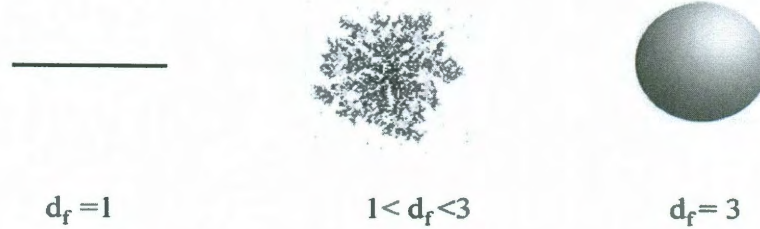


Figure 2-7 Fractal Structure at Various Fractal Dimensions

Floc fractal dimension can be measured through small angle laser light scattering (SALLS) method using a Mastersizer (Jarvis et al., 2008b). The instrument has a ring of photo-detectors at angles between  $0.01^\circ$  and  $40.6^\circ$ . The scattered light intensity  $I(Q)$  is a function of  $Q$  ( $\text{m}^{-1}$ ), the difference in the wave number between the incident and scattered laser.  $Q$  is given by:

$$Q = \frac{4\pi \sin(\theta/2)}{\lambda} \quad \text{Eq. 2-31}$$

Where  $n$ : refractive index of the suspending medium;

$\theta$ : scattered angle;

$\lambda$ : wavelength of the radiation in vacuum.

For independently scattering aggregates,  $I(Q)$  is related to  $Q$  and  $D_f$  (fractal dimension):

$$I(Q) \propto Q^{-D_f} \quad \text{Eq. 2-32}$$

The  $D_f$  can be obtained through the plot of Eq. 2-32 on a log-log scale.

### **2.3.2.2. Effect of Floc Size and Fractal Dimension on Specific Cake Resistance**

The specific cake resistance during microfiltration of coagulated water is determined by two parameters simultaneously: floc size and fractal dimension. It was shown that the specific cake resistance decreases upon increasing the aggregate size and decreasing the fractal dimensions for a synthetic system containing hematite and humic acid (Lee et al., 2003b, Lee et al., 2005b, Park et al., 2006a). Through a model calculation, Park et al. (2006a) showed that the reduction in inter-aggregate porosity is more important than that in intra-aggregate porosity during the cake collapsing process.

While the specific cake resistance can be simply determined by the floc size and fractal dimension, the floc size and fractal dimension are determined by a range of factors including coagulation mechanism, coagulant dose, flocculation time, organic content and so on. Coagulation via the charge neutralization mechanism was shown to produce more porous flocs than that under sweep flocculation conditions (Lee et al., 2000); Longer flocculation time produce larger and more open flocs, which cause lower specific cake resistance (Cho et al., 2006); Coagulation of higher humic content water creates more open flocs, which are easier to be compressed (Choi et al., 2008); Fulvic acid fraction produce the most compact and smallest flocs; humic acid fraction produce the most open floc (Sharp et al., 2006a); Sharp et al. (2006b) found that small DOC to Fe coagulant ratio leads to larger flocs while large DOC to Fe coagulant ratio produces smaller flocs; The flocs formed by preformed Al species are smaller than those formed by conventional Al salt (Shi et al., 2007); Using SALLS method, Wang et al. (2008) indicate that aluminum chloride hydrate and PACl generate more compact flocs than alum; but

McCurdy et al. (2004) contrarily showed that alum produce flocs with higher fractal dimension using an image analysis method.

## **2.4. Polymer Flocculants**

### **2.4.1. Polymer Flocculants in Drinking Water Treatment**

Polymer flocculants or coagulant aids are normally water soluble macromolecular compounds that can enhance flocculation. Several benefits can be achieved by using polymer flocculants : (1) improved effluent water quality from the granular media filters, especially high-rate (e.g., rapid sand) filters; (2) lower alkalinity consumption compared to hydrolyzing metal salts (HMS) coagulants; and (3) reduced sludge handling and disposal problems (Kim et al., 2001). Polymer flocculants can generally be characterized into two categories: natural and synthetic. The natural polymer flocculants include starches, gura gum, tannins, chitosan, and sodium alginate and so on. The advantages of natural polymer flocculants are that they are harmless and eco-friendly. However, natural polymer flocculants are rarely used because of their low efficiency in flocculation. Some common synthetic polymer flocculants used in drinking water treatment are listed in Table 2-5.

Table 2-5 Common polymer flocculants in drinking water treatment

Category	Polymer	Structure
Cationic Polymers	Poly(diallyldimethyl ammonium) Chloride	
	Epichlorohydrin/Dimethylamine	
	Cationic Polyacrylamide	
Anionic Polymers	Poly(acrylic-co-acrylamide)	
Neutral polymers	Neutral Polyacrylamide	

Source: (Bolto et al., 2007)

#### 2.4.2. Flocculation by Polymer Flocculants in Water Treatment

Polymer flocculants play an important role in controlling the size, structure and hence strength of floc particles. They are believed to increase floc size and strength and hence improve particle removal by sedimentation. Bridging, the mechanism in which

particles attach to segments of polymer molecules adsorbed on other particles, is usually considered more effective to induce flocculation than charge neutralization. Therefore, molecular properties (e.g., sign of charge, charge density, molecular weight and molecular structure) that maximize bridging usually lead to larger and stronger flocs (Bolto and Gregory, 2007). With similar molecular weight, polymer flocculants of medium charge density results in the most particulate removal than polymer flocculants of high and low or none charge density. Because polymer flocculants of high charge density commonly induce electrostatic patch flocculation and polymer flocculants of medium charge normally brings bridging flocculation, which produces stronger bonding between polymers and particulates. On the other hand, low or none charge density polymer flocculants tend to assume a coiled conformation, therefore, low or none charge density polymer flocculants have lower bonding capacity than polymer flocculants of medium charge density (Gill and Herrington, 1988, Gray and Ritchie, 2006, Smithpalmer et al., 1994) When the charge densities are the same, polymer flocculants of larger molecular weights produced larger flocs (Gill and Herrington, 1988) . With similar molecular weights, branched polymer produced larger and stronger flocs than linear polymer in a coagulation of kaolin suspension (Mpofu et al., 2003).

#### **2.4.3. Membrane Fouling by Macromolecules**

Polymer flocculants are high molecular weight organic compounds. When carried over to membrane filters residual polymers can potentially foul the membranes. The flocs containing polymers may also foul the membrane more than those formed in the absence of polymers. Although there is no research on the membrane fouling by free

polymer flocculants to date to our knowledge, fouling of microfiltration or ultrafiltration membrane by various macromolecules such as proteins and polysaccharides have been intensively studied (de Lara and Benavente, 2009, Guell and Davis, 1996, Kanani et al., 2008, Katsoufidou et al., 2007, Lin et al., 2008b, Loh et al., 2009, Susanto and Ulbricht, 2005, Ye et al., 2005, Zator et al., 2009). These macromolecules have been found to foul microfiltration and ultrafiltration membranes with pores much larger than the macromolecules themselves by accumulating both inside membrane pores and on the membrane surface. Internal fouling, i.e., foulant accumulation in the membrane pores, is usually attributed to macromolecule adsorption due to electrostatic, hydrophobic interactions and hydrogen bonding (Li and Elimelech, 2004, Nakamura and Matsumoto, 2006, Yamamura et al., 2008); it has been demonstrated by flux and hydraulic resistance analysis (Guell and Davis, 1996), measurement of streaming potential across the membrane (de Lara and Benavente, 2009, Nakamura and Matsumoto, 2006), and confocal laser scanning microscopy (CLSM) (Zator et al., 2009). Using CLSM, Zator et al. (2009) showed that microfiltration of ternary or binary solutions of BSA, dextran, and tannic acid resulted in an internal fouling layer 1 to 3  $\mu\text{m}$  deep from the membrane surface. Macromolecules such as BSA were also found to form aggregates in the feed solution (Maruyama et al., 2001); these aggregates could block membrane pores and subsequently allow deposition of more monomers and aggregates to form a multilayer cake (Kanani et al., 2008). The fouling mechanisms of dextran and other macromolecules were found to be similar to BSA (Guell and Davis, 1996, Katsoufidou et al., 2007, Loh et al., 2009, Susanto and Ulbricht, 2005, Ye et al., 2005). Water treatment polymers are

macromolecules with many properties similar to proteins and polysaccharides. However, their membrane fouling potential has not been carefully evaluated.

#### **2.4.4. Effect of Polymer Flocculants on NOM Removal**

Polymer flocculants are commonly used in the coagulation/flocculation process as coagulation aids or flocculants to increase floc size and strength, reduce alkalinity consumption, and aid sludge handling and disposal (Bolto and Gregory, 2007, Gray and Ritchie, 2006, Jin et al., 2003, Taylor et al., 2002, Zhao, 2004). However, its use in microfiltration systems has not been carefully evaluated. The effect of polymers on NOM removal has been controversial. A number of studies have shown positive impact of polymer flocculants on NOM removal. Using high dosage of alum and pDADMAC with high charge density, improved DOC and UV<sub>254</sub> absorbance removal was observed by Chang et al. (2005) during coagulation of synthetic water containing humic acids, tannic acids, and p-hydroxybenzoic acid. Non-ionic polyacrylamide and aluminum sulphate were used in the study of Jarvis et al. (2008b). The DOC removal rate was enhanced from 46% to 64% corresponding to a polymer dosage range of 0-0.25 mg/L, but almost no additional removal of UV<sub>254</sub> absorbance was observed. Lee et al. (2006) showed that positively charged pDADMAC was able to improve DOC and UV<sub>254</sub> removal when alum dosage was low, but the effect of pDADMAC was offset at high alum dosages. In the research of Bolto et al. (2001), cationic pDADMAC improved the removal of color and UV<sub>254</sub> absorbance. On the other hand, negative or neutral effects of polymer flocculants were also shown by some studies. Jarvis et al. (2008a), found that pDADMAC slightly improved DOC removal rate from 83 to 87%, but reduced UV<sub>254</sub> removal rate from 93 to



90%. Chang et al. (2005) found no benefit in DOC removal using either non-ionic or cationic polyacrylamide with low charge density; insufficient dosage of pDADMAC actually increased DOC concentration in the treated water, with the increase more than that from the over-dosage of cationic and non-ionic PAM. In addition, pDADMAC was unable to remove hydrophilic NOM (Bolto et al., 2001), a major contributor to microfiltration membrane fouling (Carroll et al., 2000, Chen et al., 2007).

#### **2.4.5. Effect of Polymer Flocculants on Floc Properties**

Past investigations on the effect of polymer flocculants on floc structure have primarily focused on clay flocculation (Ammery and Cleasby, 2004), not many studies could be found for natural surface water. In fact, no studies have systematically investigated the effect of polymer flocculants on floc structure during coagulation of surface water as of now. The effect of polymer flocculants on floc structure during coagulation of surface water is inconclusive. Cationic pDADMAC has been shown to increase both size and fractal dimension of flocs in polyferric chloride of humic substances (Wei et al., 2009); neutral polyacrylamide increased the floc size but decreased floc fractal dimension in a coagulation of surface water using alum (Jarvis et al., 2008b). But no increase in floc size was found by cationic pDADMAC in other studies of Jarvis et al. (2008a, 2006) during their coagulation of surface water using ferric chloride. The significant difference between these studies can be caused by various factors: coagulation condition, coagulant type, properties of polymer flocculants (charge and size), water quality and so on.

## 2.5. Conclusions

Although polymers bring several advantages as flocculants during conventional water treatment (coagulation, flocculation, and sedimentation) such as lower dosage requirement of coagulant, reduced consumption of alkalinity, and better floc structure in terms of floc sedimentation (Bolto and Gregory, 2007), there are several uncertainties about using polymer flocculants in the coagulation-microfiltration system as elaborated above: (1) polymer flocculants are macromolecules and therefore may foul the membrane themselves when overdosed; (2) polymer flocculants do not necessarily help removal of NOM and turbidity, because NOM is primarily removed through charge neutralization or adsorption by inorganic coagulant, and microfiltration membranes have pores that are small enough to screen the floc particles for turbidity removal; (3) Polymer flocculants could bring changes to floc and cake layer structure, which in turn bring different resistance to microfiltration. Therefore, there is a need to systematically investigate the role of polymer flocculants in the coagulation-microfiltration of surface water.

## ***Chapter 3 Methodology***

### **3.1. Hypothesis and Critical Parameters**

In a coagulation-microfiltration system, polymer flocculants are hypothesized to affect membrane performance (membrane fouling & contaminant removal) through several ways: (1) affect NOM removal in the coagulation process; (2) affect NOM removal through changing cake layer structure (3) directly foul the membrane when polymers are over dosed; (4) affect membrane fouling through changing floc properties (size, fractal dimension, and stickiness) and thus cake layer structure. As discussed in the literature review section, a series of factors can significantly affect the performance of microfiltration including membrane properties, surface water quality, and operation mode etc.. In addition, polymers of different properties (e.g. charge and size) are hypothesized to affect both the coagulation/flocculation process and microfiltration process. In this research, the above hypotheses were tested and verified to understand the role of polymer flocculants in the coagulation-microfiltration system. Parameters such as membrane type, surface water quality, polymer type, and operation mode were considered as well. The detailed methodology of this research is depicted in the following section.

### **3.2. Methodology**

Investigations of the impact of polymer flocculants were developed on the basis of the four hypotheses.

### **3.2.1. Effect of Polymer Flocculants on Contaminant Removal in Coagulation/Flocculation**

To investigate the effect of polymer flocculants on contaminant removal in coagulation/flocculation process, coagulation/flocculation of two surface waters with significantly different quality were carried out with different polymer flocculants.

The two waters used are Mississippi river water sampled from Minneapolis of Minnesota and the Grand lake water sampled from Vinita of Oklahoma. The Mississippi river water has a high DOC and turbidity concentration while the Grand lake water has a medium DOC and turbidity concentration. Polyaluminum chloride was used as primary coagulant due to the stability of its species under various conditions. Three kinds of polymer flocculants of different properties were employed including positively charged polydiallyldimethylammonium chloride (pDADMAC), neutral polyacrylamide (PAM), and negatively charged poly (acrylic-co acrylamide).

The coagulated/flocculated waters were sampled for turbidity, DOC,  $UV_{254}$ , and HPSEC (High Performance Size Exclusion Chromatography) analysis to understand the effect of polymer flocculants on contaminant removal. In addition, flocs from coagulation of the two waters were analyzed for size and fractal dimension. Because cake layer structure is directly related to floc size and fractal dimension, understanding of the effect of polymer flocculants on floc properties helps understanding of the effect of polymer flocculants on cake layer structure and membrane fouling brought by cake layer.

Details and results of this investigation are presented in Chapter 5 — “Impact of Polymer Flocculants on Microfiltration of Surface Water—Part I: Coagulation Pretreatment”

### **3.2.2. Direct Fouling of Microfiltration Membrane by Overdosed Polymer Flocculants**

To investigate the direct fouling of microfiltration membrane by overdosed polymer flocculants, synthetic water was prepared for flat sheet microfiltration under various conditions. The synthetic water contains only polymer flocculants and background salts, and membranes of three different materials were tested. Synthetic water was intended to avoid unnecessary interference from other elements in the natural surface water.

The same polymer flocculants described in the previous section were used in this investigation. The primarily tested concentration of polymer flocculants tested is 0.1 mg/L. Normally, the concentration of polymer flocculants used in a microfiltration plant is around 1 mg/L. Therefore, a 0.1 mg/L concentration is considered reasonable to represent the residual polymer flocculant in the coagulated water. Polymer flocculants of 0.05 mg/L and 0.5 mg/L were also tested to evaluate the effect of polymer concentration on membrane fouling. The background salt used was primarily 10 mM NaCl, which has a similar ionic strength to normal surface water. The effect of divalent cation on microfiltration membrane fouling was evaluated by using 7mM NaCl+1mM CaCl<sub>2</sub>, which has a total ionic strength of 10mM as well. In addition, the synthetic water was adjusted to three pHs (4, 7, and 10) to evaluate the effect of pH on membrane fouling by polymer

floculants. Three types of commercial membranes were used in this investigation: modified polyvinylidene fluoride (PVDF), polyethersulfone (PES), and polysulfone (PS). The three membranes were used because their wide usage in industry.

Details and results of this investigation can be found in Chapter 4 — “Fouling of Microfiltration Membranes by Organic Polymer Coagulants and Flocculants”.

### **3.2.3. Effect of Polymer Flocculants on NOM Removal and Membrane Fouling**

The impacts of polymer flocculants on NOM removal and membrane fouling were investigated through coagulation/flocculation-microfiltration of the two surface waters. The surface waters, coagulants, polymer flocculants used were the same as those described in section 3.2.1. Different operation conditions were employed in this investigation including flat sheet membrane and hollow fiber membrane filtration, direct filtration, inline filtration, and filtration with sedimentation. In addition, constant flow rate microfiltration was used to be consistent with industrial application.

The pressure difference across the membrane (transmembrane pressure, (TMP)), DOC, and  $UV_{254}$  were monitored for evaluating the effect of polymer flocculants on NOM removal and membrane fouling. The details and results of this investigation are presented in Chapter 6 — “Impact of Polymer Flocculants on Microfiltration of Surface Water—Part II: Membrane Filtration”

### **3.2.4. Effect of Polymer Flocculants on Floc Properties and Cake Layer Structure**

In a coagulation/flocculation-microfiltration system, both residual free polymers after coagulation and cake layer formed on the membrane surface contribute to membrane fouling. The direct fouling of microfiltration membrane by polymer flocculants was investigated through synthetic water filtration using flat sheet membrane filtration as elaborated in section 3.2.2. The method for investigating the effect of polymer flocculants on membrane fouling caused by changing cake layer on membrane surface is described in this section.

It is hypothesized that polymer flocculants can vary cake layer structure through changing floc properties (size, fractal dimension, and stickiness); In addition, residual free polymers in the coagulated water due to overdose might also be distributed in the cake layer and membrane surface, the residual free polymer in the cake layer might increase the density of the cake layer while the residual free polymer on the membrane surface can increase the attachment of flocs and other contaminant.

Two membrane reactors were designed for this investigation: a cross flow flat sheet membrane reactor and a detachable hollow fiber membrane reactor. With the cross flow flat sheet membrane reactor, the impact of polymer flocculants on floc stickiness was evaluated by circulating the coagulated water through the reactor under two conditions: attachment of flocs generated by primary coagulant (PACl) only onto polymer coated flat sheet membrane and attachment of flocs generated from both primary coagulant and polymer flocculants onto clean membrane surface. Measurement of mass



of flocs accumulated on membrane surface, imaging of fouled membrane surface, and filming of membrane fouling by flocs under conditions with/without polymer flocculants were carried out.

Two investigations were performed with the hollow fiber membrane reactor as well: (1) polymer concentration on the fouled membrane surface at different filtration cycles; (2) the cake layer structure on the membrane surface with/without polymer flocculants. Hollow fiber membrane filtrations were first performed using Lake Houston water and the same coagulant and polymer flocculants as described before. The fouled membrane fibers were sampled after different filtration cycles and subjected to Attenuated Total Reflectance-Fourier Transform InfraRed analysis for a possible change in the polymer flocculation concentration after different filtration cycles. In addition, the fouled membrane samples were specially treated for imaging by Scanning Electron Microscope (SEM) to observe a possible change of the cake layer structure.

Details and results of this investigation were presented in Chapter 7 — “Impact of Polymer Flocculants on Floc Properties and Cake Layer Structure”

***Chapter 4 Fouling of Microfiltration  
Membranes by Organic Polymer Coagulants  
and Flocculants<sup>1</sup>***

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<sup>1</sup> This chapter is modified from “Wang, S., Liu, C. and Li, Q. (2011) Fouling of microfiltration membranes by organic polymer coagulants and flocculants: Controlling factors and mechanisms. Water Research 45(1), 357-365”

## 4.1. Introduction

Microfiltration (MF) has been increasingly applied to drinking water and wastewater treatment due to the small footprint, superior treated water quality, and high level of automation compared to conventional treatment processes. Major limitations of the MF technology include inefficiency in natural organic matter (NOM) removal (Vickers et al., 1995), and membrane fouling. Many source waters contain significant amount of NOM—a precursor of harmful disinfection byproducts. In addition, membranes can be fouled by NOM over time, leading to loss in water production and requiring more frequent cleaning. As a result, coagulation/flocculation is often used as pretreatment to increase NOM removal and to control membrane fouling.

Polymers are widely employed in the coagulation/flocculation process in conventional water treatment systems (Bolto and Gregory, 2007). They are known to improve effluent water quality by increasing floc size and strength, reduce alkalinity consumption, and alleviate sludge handling and disposal problems (Gray and Ritchie, 2006, Jin et al., 2003, Taylor et al., 2002, Zhao, 2004). Therefore, polymers are also adopted in the coagulation/flocculation pretreatment process for many MF systems (Nozic et al., 2001). However, it is unclear whether the use of polymers in MF systems is beneficial. Firstly, MF membranes can remove significantly smaller particles than those removed by the conventional treatment process; the use of polymers may not have measurable effect on turbidity removal. Secondly, the effect of polymers on NOM removal has been controversial. Although a number of studies reported improved NOM removal when polymers were used (Jarvis et al., 2008b, Kim and Walker, 2001, Lee and

Westerhoff, 2006), others reported no or negative impact of polymers on NOM removal (Chang et al., 2005, Jarvis et al., 2006). Finally, polymers are high molecular weight (MW) organic compounds. When carried over to membrane filters residual polymers can potentially foul the membranes. The flocs containing polymers may also foul the membrane more than those formed in the absence of polymers. Therefore, the effect of polymers on membrane performance needs to be carefully assessed for system optimization.

Fouling of MF or UF membrane by various macromolecules such as proteins and polysaccharides have been intensively studied (de Lara and Benavente, 2009, Guell and Davis, 1996, Kanani et al., 2008, Katsoufidou et al., 2007, Lin et al., 2008b, Loh et al., 2009, Susanto and Ulbricht, 2005, Ye et al., 2005, Zator et al., 2009). These macromolecules have been found to foul MF and UF membranes with pores much larger than the macromolecules themselves by accumulating both inside membrane pores and on the membrane surface. Internal fouling, i.e., foulant accumulation in the membrane pores, is usually attributed to macromolecule adsorption due to electrostatic, hydrophobic interactions and hydrogen bonding (Li and Elimelech, 2004, Nakamura and Matsumoto, 2006, Yamamura et al., 2008); it has been demonstrated by flux and hydraulic resistance analysis (Guell and Davis, 1996), measurement of streaming potential across the membrane (de Lara and Benavente, 2009, Nakamura and Matsumoto, 2006), and confocal laser scanning microscopy (CLSM) (Zator et al., 2009). Using CLSM, Zator et al. (2009) showed that MF of ternary or binary solutions of BSA, dextran, and tannic acid resulted in an internal fouling layer 1 to 3  $\mu\text{m}$  deep from the membrane surface. Macromolecules such as BSA were also found to form aggregates in the feed solution

(Maruyama et al., 2001); these aggregates could block membrane pores and subsequently allow deposition of more monomers and aggregates to form a multilayer cake (Kanani et al., 2008). The fouling mechanisms of dextran and other macromolecules were found to be similar to BSA (Guell and Davis, 1996, Katsoufidou et al., 2007, Loh et al., 2009, Susanto and Ulbricht, 2005, Ye et al., 2005). Water treatment polymers are macromolecules with many properties similar to proteins and polysaccharides. However, their membrane fouling potential has not been carefully evaluated.

The study reported here systematically investigated the impact of free polymers (i.e., those not bound to a floc) on membrane fouling. The roles of polymer molecular characteristics, MF membrane properties, and solution conditions of feed water were evaluated and the fouling mechanism was elucidated. The use of polymers in conjunction with a hydrolyzing metal salt as the primary coagulant for MF of surface water will be addressed in a separate publication.

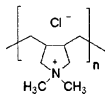
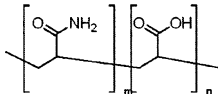
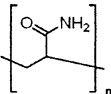
## **4.2. Materials and methods**

### **4.2.1. Polymers and membranes**

Three types of polymers commonly used in water treatment are tested in this study: poly(diallyldimethylammonium) chloride (pDADMAC), poly(acrylic acid-co-acrylamide) (PACA), and polyacrylamide (PAM). To avoid interference from additives and impurities commonly found in commercial water treatment polymers, analytical grade polymers were purchased from Sigma Aldrich (St. Louis, MO). Relevant

characteristics of these polymers are listed in Table 4-1. It is noted that the two PACA polymers have different monomer composition: The 520 kDa PACA contains 80% acrylamide and 20 % acrylic acid, while the 200 kDa PACA contains 20% acrylamide and 80 % acrylic acid.

Table 4-1 Polymers used in this investigation

Polymer	pDADMAC	PACA	PAM
Molecular structure			
Ionic property	Cationic	Anionic	Non-ionic
MW (kDa)*	<100, 100-200 200 - 350, 400 -500	200 520	5,000 - 6,000

\* Provided by the supplier (Sigma Aldrich, St. Louis, MO)

Electrophoretic mobility and hydrodynamic diameter of each polymer were determined by phase analysis light scattering (PALS) and dynamic light scattering (DLS), respectively, using a Zen3600 Zetasizer (Malvern Ltd., Malvern, UK) under the same solution conditions as those used in the filtration experiments described later. DLS measurements were initially performed with various polymer concentrations to determine

an appropriate concentration. A concentration of 1 g/L was found to provide sufficient light scattering for the measurement.

Three types of MF membranes, denoted MF-1, MF-2, and MF-3, and made of modified polyvinylidene fluoride (PVDF), polyethersulfone (PES) and polysulfone (PS), respectively (Pall Corporation, East Hills, NY), were employed in this study. Two batches of MF-1 membrane were used. The first batch was named MF-1 and the second batch was named MF-1a. All three types of membranes have a nominal pore size of 0.2  $\mu\text{m}$ . Flat sheet membranes were cut into circular coupons of 2.5-cm diameter and stored at 4 °C in ultrapure water generated by a Barnstead Epure purification system (Barnstead Thermolyne, IA, USA). The storage water was changed weekly. Surface zeta potential of the membranes was determined using a ZetaCAD streaming potential analyzer (CAD Instrumentation, Les Essarts-le-Roi, France) under the same solution conditions used in the filtration experiments.

#### **4.2.2. Feed water**

Synthetic feed water was prepared using the aforementioned ultrapure water. The feed water used in all experiments had an ionic strength of 10 mM made of either 10 mM NaCl or 7 mM NaCl and 1 mM  $\text{CaCl}_2$ . The concentration of polymers in the feed water was 0.05, 0.1, or 0.5 mg/L. These concentrations were chosen to represent the possible concentration range of the free polymer molecules carried over from the coagulation/flocculation basin to the membrane reactor. 0.1 M HCl, 0.1 M NaOH, and 0.001 M  $\text{Na}_2\text{HPO}_4$  were used to adjust the solution pH to 4, 7 and 10.

### 4.2.3. Membrane filtration experiments

Membrane filtration experiments were performed with a bench-scale dead-end filtration system in a constant-flux mode. The schematic of the experimental setup is shown in Figure 4-1. A Filtrtec peristaltic pump (SciLog, Middleton, WI) fed the water from a 4 liter reservoir to a 10 mL Amicon stirred cell (Millipore, Billerica, MA), where the membrane sample was housed. Two pressure sensors, located immediately upstream and downstream of the filtration cell, measured the pressures of the feed and filtrate streams. Membrane filtrate was collected in a container on a bench-top electronic balance, which measured the cumulative mass of filtrate for calculation of membrane flux. The pump and the balance were interfaced with a lab PC to collect data of the measured flux and trans-membrane pressure. In every filtration experiment, ultrapure water was first filtered for 10 minutes; synthetic feed water spiked with the desired polymer concentration was then filtered through the membrane for 60 minutes. The initial trans-membrane pressure (TMP) in all experiments was controlled at 10 psi and the corresponding operating flux was  $1.10 \times 10^{-3}$ ,  $2.55 \times 10^{-3}$  and  $1.36 \times 10^{-3}$  m/s (3973, 9167 and 4889 LMH) for MF-1, MF-2 and MF-3, respectively. All experiments were run at a feed water temperature of 22 °C and were repeated at least once. A new membrane coupon was used for every filtration experiment. TMP at the end of each filtration was normalized with respect to the initial TMP and used as the measure for membrane fouling rate, the normalized TMP was named as NTMP.



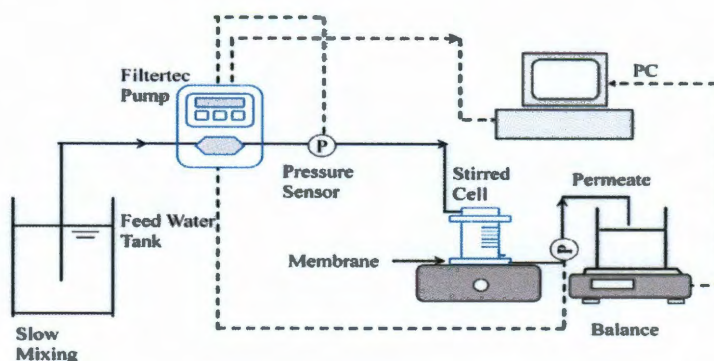


Figure 4-1 Schematic of synthetic water filtration setup

#### 4.2.4. Scanning electron microscopy (SEM) characterization of clean and fouled membranes

Field Emission scanning electron microscope (FEI Company, Philips XL30) was used to characterize the MF membranes before and after filtration of the ultrapure water and the polymer containing feed water. Membrane samples after filtration were carefully removed from the filtration cell and air dried. Both top surface and cross-section of the membranes were analyzed. For cross-section imaging, the fouled membrane samples were first cut into thin strips. A small incision was made on each long side of the strip along the line where the cross-section was to be imaged. One end of the membrane strip was then dipped into liquid nitrogen for at least 10 seconds, leaving the incisions just above the liquid nitrogen surface. When taken out from the liquid nitrogen, the frozen membrane sample was immediately cleaved by a gentle tap near the incisions using a pair

of clean forceps. This method provides a clean cut exposing the cross-section of the membrane sample while preserving the structure of the fouling layer. Membrane surface porosity and pore size distribution were determined by analyzing surface images using the Image J software (Nation Institute of Health).

## **4.3. Results and discussion**

### **4.3.1. Characterization of membranes and polymers**

The surface zeta potentials of the three membranes at three different pH values are presented in Figure 4-2. All three membranes are negatively charged in the pH range of 4 -10, and the negative charge increased with increasing pH. The magnitude of the negative zeta potential of the membranes follow the order of MF-3 (PS) < MF-1 (PVDF) < MF-2 (PES) over the pH range tested. Membrane permeability was determined by clean water flux measurement over a pressure range of 5 to 50 psi and was  $1.4 \times 10^{-8}$ ,  $1.21 \times 10^{-8}$ ,  $3.71 \times 10^{-8}$ , and  $2.09 \times 10^{-8}$  m/s-Pa (347, 300, 921, and 520 LMH/psi) for MF-1, MF-1a, MF-2 and MF-3, respectively. SEM images of the clean membranes are presented in Figure 4-9.

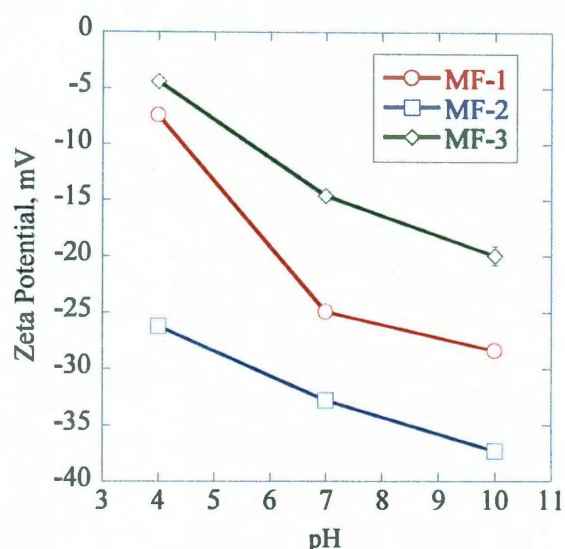


Figure 4-2 Membrane surface zeta potential as a function of pH.

Polymer molecular size was characterized by hydrodynamic diameter. Figure 4-3 shows the intensity based particle size distribution of the polymers. Each distribution is an average of at least 7 measurements. All polymers except the 520 kDa PACA exhibit a bimodal or multi-modal size distribution. The peaks at the larger size positions are attributed to high MW impurities or aggregate formation at the concentration used for size measurement, i.e., 1 g/L. It is noted that the intensity of light scattered by a particle is proportional to the sixth power of its diameter (Xu, 2002). Therefore, the apparently large peaks for the larger sizes represent only a small number of molecules or aggregates. The peak of the smaller size represents the size of individual polymer molecules, which accounts for the majority of the particles detected.



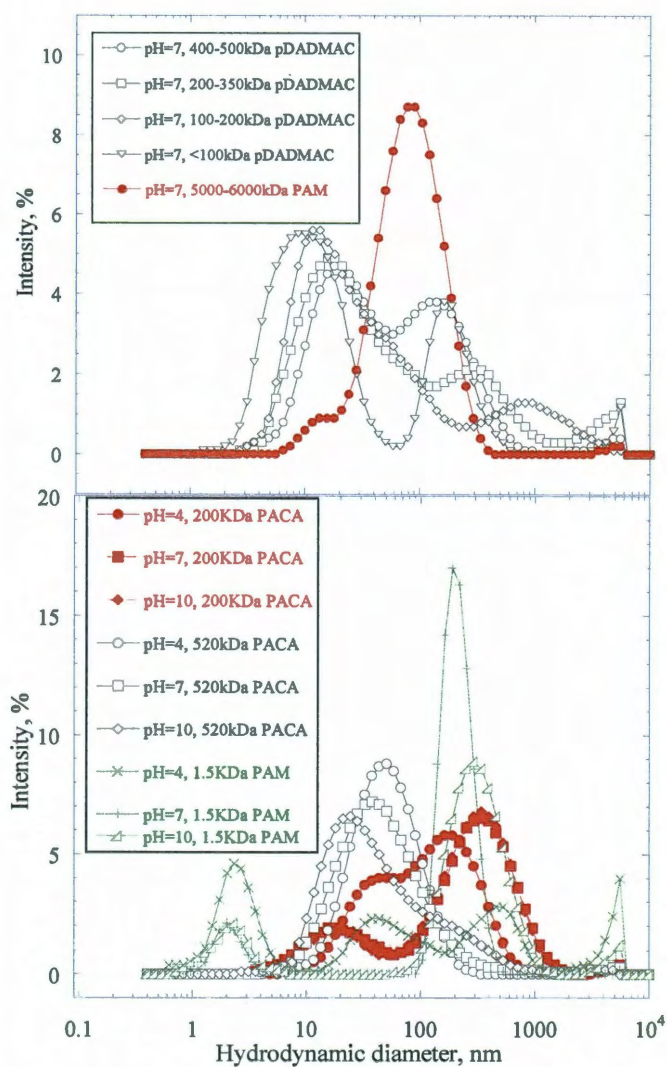


Figure 4-3 Molecular size distribution: (a) pDADMACs and 5000-6000kDa PAM at pH 7; (b) 1.5kDa PAM, 200kDa and 520kDa PACA at pH 4, 7, and 10.

The size distributions of the four pDADMACs and the 5000-6000kDa PAM were independent of solution pH. Therefore, only the distributions at pH 7 were presented in Figure 4-3 (a). The particle sizes of the four pDADMACs follow the same order as their MW. The 5000-6000kDa PAM was much larger than the pDADMACs. Solution pH had significant impact on the molecular and aggregate sizes of PACAs and the 1.5 kDa PAM

(Figure 4-3 (b)). At pH 7 and 10, the 200 kDa PACA showed a primary peak at ~20 nm; this peak shifted to ~40 nm at pH 4. This was attributed to aggregate formation due to the lower electrostatic repulsion and the formation of hydrogen bond at low pH. The size of the 520 kDa PACA also increased with decreasing pH, suggesting aggregation at lower pH. The molecular size of the 1.5 kDa PAM was much smaller than the rest of the polymers (~2 nm), consistent with its low MW.

Figure 4-4 shows the electrophoretic mobility of the polymers as a function of pH. All pDADMAC molecules were highly positively charged and the electrophoretic mobility was constant over the pH range tested. This is consistent with their quaternary amine functionality. The 5000-6000 kDa PAM showed near-zero electrophoretic mobility at all measured pH values. The 1.5 kDa PAM, however, was slightly positively charged at low pH and negatively charged at higher pH, possibly due to the presence of carboxyl and amino functionalities originated from hydrolysis of the amide groups. Both the 200 kDa and the 520 kDa PACA were negatively charged at all pHs measured due to deprotonation of carboxyl groups. The higher content of acrylic acid units in the 200 kDa PACA is responsible for its higher negative electrophoretic mobility than that of the 520 kDa PACA.

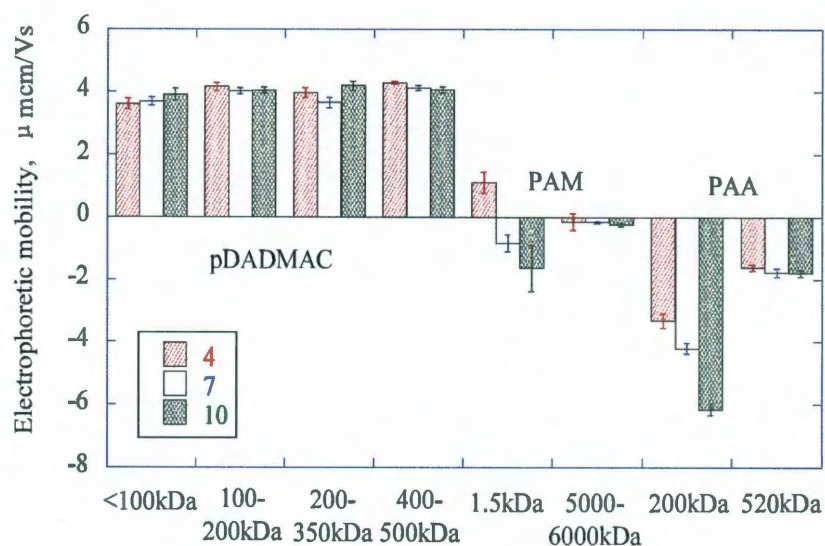


Figure 4-4 Polymer electrophoretic mobility at pH 4, 7, and 10

### 4.3.2. MF Membrane Fouling by Polymers

In general, all polymers except the 1.5 kDa PAM caused significant fouling of all three MF membranes at a concentration as low as 0.05 mg/L. The effects of the polymer MW, polymer and membrane surface charge, solution condition and polymer concentration are described in details below.

#### 4.3.2.1. Effect of polymer MW

Among the various factors investigated, polymer MW had the greatest impact on MF membrane permeability. Figure 4-5 demonstrates the effect of the polymer MW on fouling of the MF-1 membrane by pDADMAC and PAM at the feed concentration of 0.1 mg/L. The TMP at the end of the 60 min filtration increased significantly with increasing MW of pDADMAC and PAM. Only slight fouling was observed with the <100 kDa

pDADMAC and the 1.5 kDa PAM: 6.8-8.7% and 0.7-1.7 % increase in TMP respectively. The higher MW polymers, on the other hand, caused much more severe fouling: At the end of the 60 min filtration, the TMP rose by 130% and 60% for the 400-500 kDa pDADMAC and the 5000 – 6000 kDa PAM, respectively. Similar effects of MW were observed for MF-2 and MF-3 membranes (data not shown).



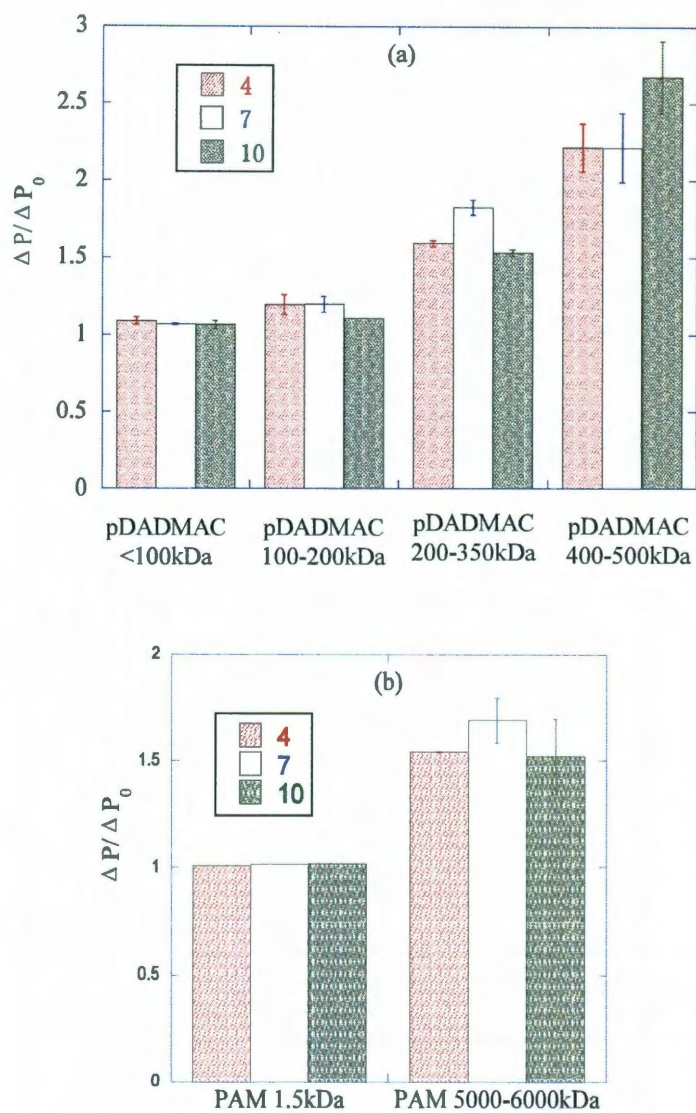


Figure 4-5 Effect of polymer molecular weight on membrane fouling by (a) pDADMAC, and (b) PAM. Feed water contains 10mM NaCl and 0.1 mg/L of polymers

#### 4.3.2.2. Effect of Polymer and Membrane Surface Charge

Charge of the polymer molecules was also found to play an important role in fouling of MF membranes. Figure 4-6 (a) compares the normalized TMPs of the three



membranes after fouled by the 400–500 kDa pDADMAC, the 5,000–6,000 kDa PAM and the 520 kDa PACA at pH 7. The TMPs at the same permeate volume (1.95 L) were used so that the comparison was based on the same polymer load for all membranes. The cationic pDADMAC caused notably more fouling than the nonionic PAM and the anionic PACA in spite of the much higher MW of the PAM. This is attributed to the strong electrostatic attraction between the positively charged pDADMAC (Figure 4-4) and the negatively charged membrane surfaces (Figure 4-2), which leads to adsorption of pDADMAC molecules on the membrane. On the other hand, the anionic PACA caused the least fouling among the three polymers due to the electrostatic repulsion between PACA molecules and the membrane surfaces as well as the lower MW compared to the PAM.

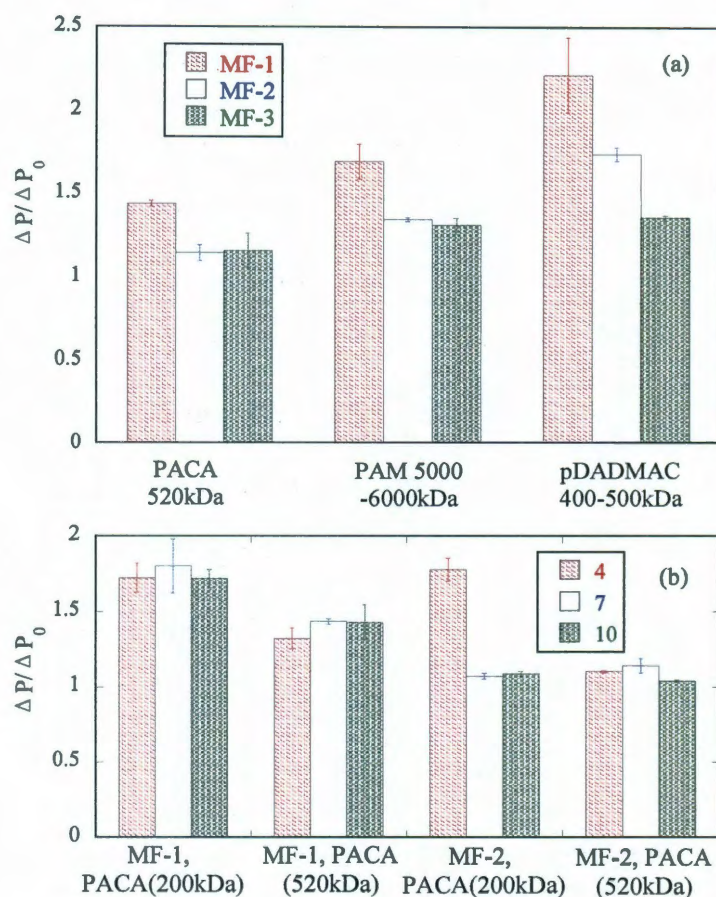


Figure 4-6 Fouling of the three MF membranes by different polymers. (a) Effect of polymer charge; (b) Effect of polymer chemical functionality. The feed water contained 10 mM NaCl and 0.1 mg/L of polymers. pH = 7. Filtrate volume for all experiments was 1.95 L

Comparison of the fouling behaviors of the three membranes suggests that mechanisms other than electrostatic interaction are also important. As shown in Figure 4-2, the MF-2 membrane had the highest negative surface zeta potential, and the MF-3 membrane the lowest. However, MF-1 experienced the most fouling by all polymers tested. One possible reason is the high surface porosity (Table 4-2) and roughness of the

MF-1 membrane (see Figure 4-9 and 4-10), which provides more surface area at the membrane pore openings for polymer accumulation and subsequent pore blockage, the main mechanism responsible for fouling by the polymers as explained later.

In addition to charge, polymer chemical functionality also played a role in membrane fouling. The 520 kDa PACA contains 80% acrylamide and 20 % acrylic acid while the 200 kDa PACA contains 20% acrylamide and 80 % acrylic acid. The difference in acrylic acid content resulted in notable difference in their fouling potential, as depicted in Figure 4-6 (b). The 200 kDa PACA consistently fouled the MF-1 membrane more than the 520 kDa PACA at all three pHs even though it has much higher negative charge and lower MW. Different results were observed with the MF-2 membrane. The two PACA polymers fouled the MF-2 membrane similarly except at pH 4, when the 200 kDa PACA showed drastically higher fouling potential: The normalized TMP reached as high as 1.78. Apparently, the fouling behavior of the 200 kDa PACA cannot be explained simply by electrostatic interaction. It is speculated that the higher rate of MF-1 fouling by the 200 kDa PACA is due to formation of aggregates through intermolecular hydrogen bonding between carboxyl groups. This is supported by the measured molecular size distribution in Figure 4-3. For the MF-2 membrane, whose surface zeta potential is much higher than that of MF-1, the stronger electrostatic repulsion between the highly negatively charged 200 kDa PACA and the membrane partly negates the effect of the aggregates, resulting in fouling potential similar to that of the 520 kDa PACA and overall less fouling than MF-1. We speculate that the severe fouling of MF-2 by the 200 kDa PACA at pH 4 may be due to hydrogen bond formation

between the carboxylic acid groups on the polymer and the sulfonyl groups on the MF-2 membrane surface.

#### **4.3.2.3. Effect of solution chemistry**

##### **4.3.2.3.1. Effect of pH**

Solution pH is usually an important factor in membrane fouling because it affects the charge of ionizable foulants (e.g., polyelectrolytes) and surface charge of the membranes. In our study, however, the effect of feed water pH was small in most cases, as shown in Figures 4-5 and 4-6 (b). For the nonionic PAM, this is due to the lack of electrostatic interaction. The charge of the cationic pDADMAC is independent of pH because the quaternary amine on the polymer does not dissociate as pH changes. The negative surface zeta potential of all membranes increases with increasing pH (Figure 4-2). In spite of the expected increase in electrostatic attraction caused by higher negative surface charge of membranes at higher pH, no consistent trend in membrane fouling by pDADMAC was observed. A possible explanation is that the attractive interaction between the highly positively charged pDADMAC and the negatively charged membranes is very strong even at the lowest pH tested; further increase in negative membrane surface charges does not cause notable changes. Similarly, the effect of pH on membrane fouling by PACA is small due to the strong electrostatic repulsion even at the lowest pH. One exception is the fouling of the MF-2 membrane by the 200 kDa PACA at pH 4, which was discussed above.

#### 4.3.2.3.2. Effect of calcium

Calcium ion has significant influence on membrane surface charge (Saravia et al., 2006), and can effectively neutralize negative charges of polyelectrolytes to form intermolecular bridging, leading to changes in polymer molecular conformation and aggregation (Hong and Elimelech, 1997, Li and Elimelech, 2004, Yuan and Zydney, 1999a). Calcium has been found to aggravate membrane fouling by bovine serum albumin (BSA) (Palecek et al., 1993)(Palecek et al., 1993) and humic acid (Bouchard et al., 1997, Costa et al., 2006, Hong and Elimelech, 1997, Li and Elimelech, 2004), as well as to increase irreversible membrane fouling by sodium alginate (van de Ven et al., 2008).

To investigate the effect of calcium, 1 mM  $\text{CaCl}_2$  was added to the synthetic feed water and NaCl concentration was reduced to 7 mM to maintain ionic strength of 10 mM. Each experiment was repeated at least five times. The results are presented in Figure 4-7(a). The presence of calcium did not change the fouling potential of pDADMAC and PAM. These results are consistent with the molecular structures of pDADMAC and PAM, which do not have functional groups that interact with  $\text{Ca}^{2+}$  specifically. The charge screening effect of  $\text{Ca}^{2+}$  was not significant enough to cause notable changes in the adsorption of pDADMAC and PAM onto membrane surface.

Calcium ions caused a very slight decrease in the fouling of the MF-1 membrane by the 520 kDa PAA. This effect is more evident with the MF-1a membrane (Figure 4-7 (b)), which has smaller pores than MF-1 as indicated by the lower permeability. The fouling of MF-1a by the 520 kDa PACA was notably less in the presence of  $\text{Ca}^{2+}$ , while

fouling by PAM or pDADMAC was not affected by  $\text{Ca}^{2+}$  (data not shown). This is attributed to the intra-molecular complexation between  $\text{Ca}^{2+}$  and carboxyl groups in PACA molecules, which leads to a more coiled and compact conformation of the PACA molecules (Peng and Wu, 1999). This change of molecular configuration was confirmed by molecular size measurement: The number-mean molecular size of the 520 kDa PACA is 12% smaller in the presence of 1 mM  $\text{Ca}^{2+}$  than that measured without  $\text{Ca}^{2+}$ . As the molecular size decreased, membrane fouling was reduced due to less pore blockage, as discussed in “**Fouling mechanism**” later.

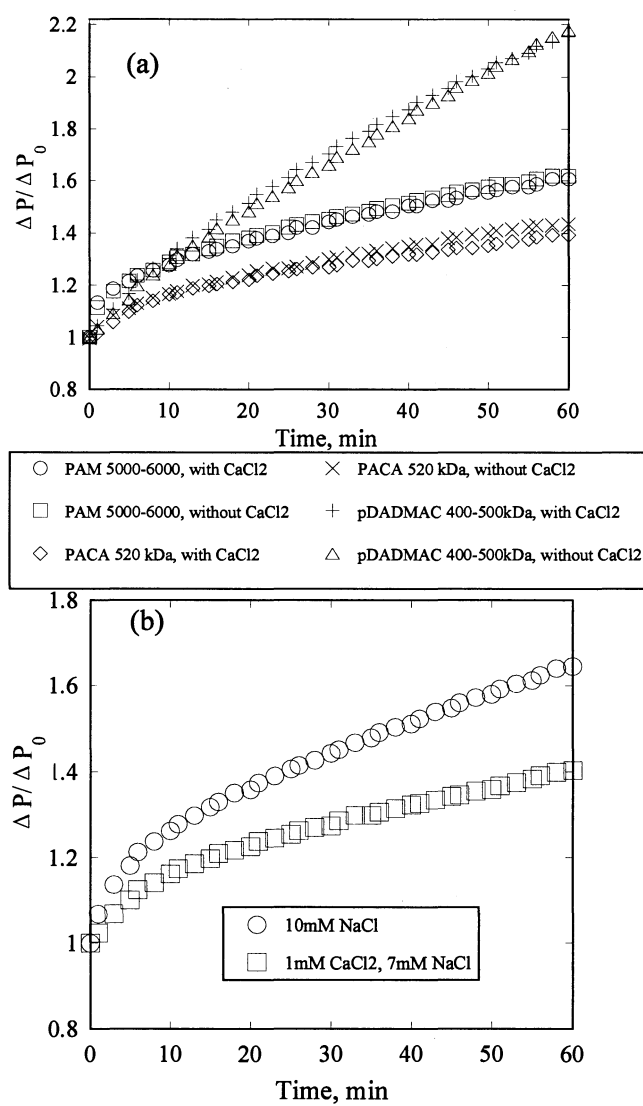


Figure 4-7 Effect of calcium ions on fouling of: (a) MF-1; (b) MF-1a by 520 kDa PAA.

pH = 7.

#### 4.3.2.4. Effect of polymer concentration

Three different concentrations of the polymer, 0.05, 0.1 and 0.5 mg/L, were used in the filtration experiments. The results for the MF-1 membrane are shown in Figure 4-8. The fouling of the membrane was unexpectedly severe, even when polymer concentration was as low as 0.05 mg/L. The extent of fouling increased greatly with increasing polymer concentration. At 0.5 mg/L, the 400-500 kDa pDADMAC and the 520 kDa PACA resulted in 420 and 243 % increase in TMP, respectively.

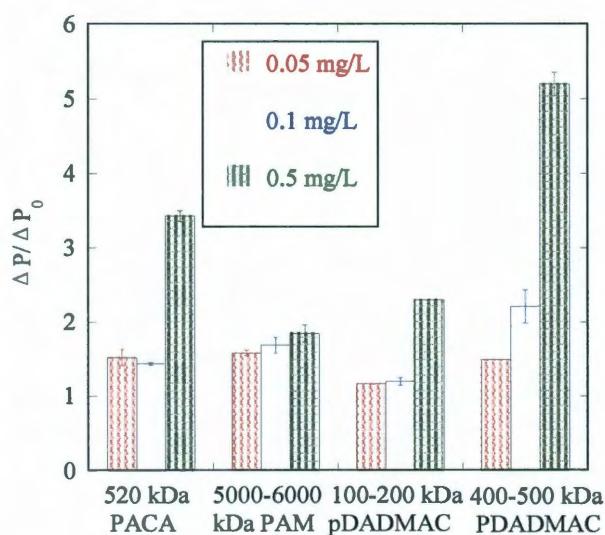


Figure 4-8 Effect of polymer concentration on MF-1 membrane fouling. The feed water contained 10 mM NaCl at pH 7.

#### 4.3.3. Fouling mechanism

MF membrane fouling is usually attributed to four mechanisms (Hermia, 1982, Hlavacek and Bouchet, 1993): (a) Constriction of membrane pores — restricting flow



by the foulants smaller than the membrane pores adsorbed onto the pore walls; (b) Complete blockage of membrane pores by the foulant — stopping both the solvent (e.g., water) and the solute (e.g., the foulant) through the blocked pores; (c) Intermediate blocking of membrane pores — restricting solute flowing through the blocked pores but allowing the solvent to go through at a lower rate; (d) Cake/gel layer formation due to accumulation of foulants.

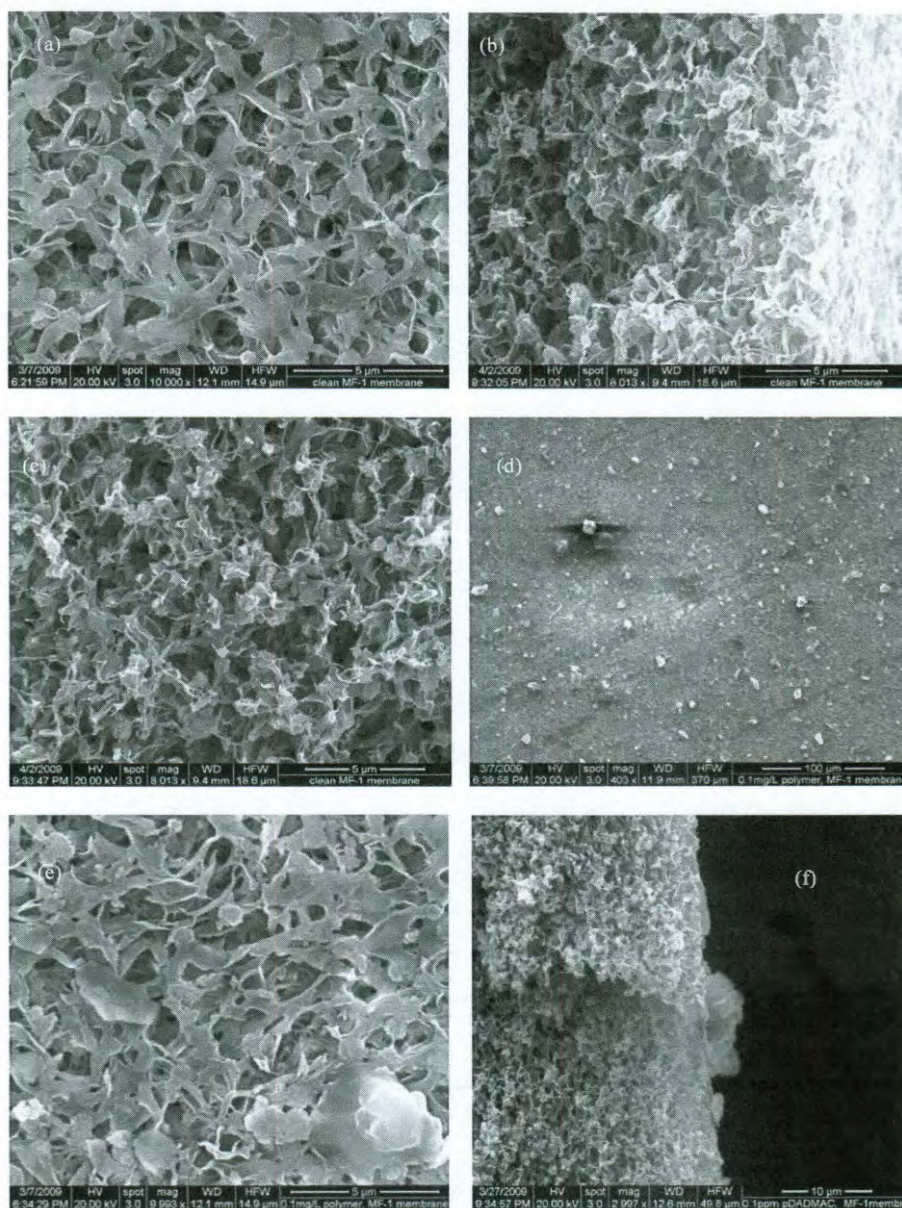
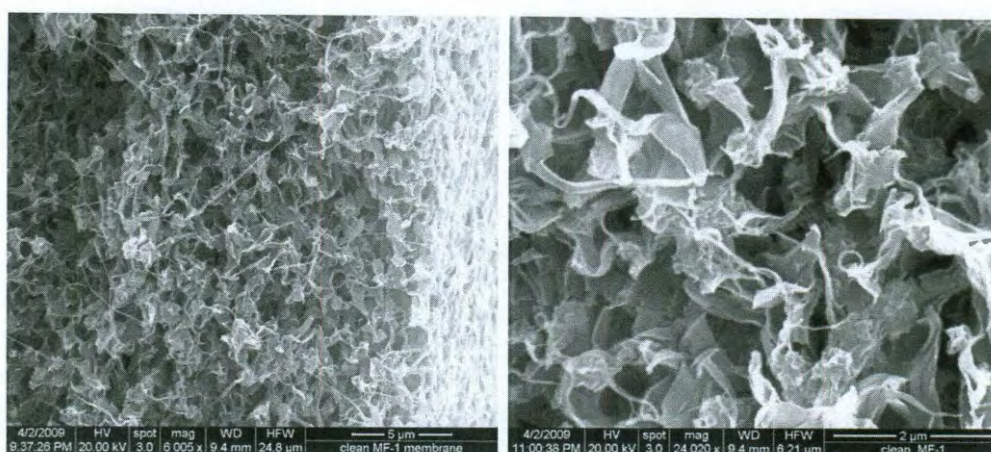


Figure 4-9 SEM images of clean and fouled MF-1: (a) clean membrane surface; (b, c) clean membrane cross sectional; (d, e) fouled membrane surface; (f) fouled membrane cross sectional. The feed water contained 10 mM NaCl, and 0.1 mg/L 400-500 kDa pDADMAC. pH = 7.

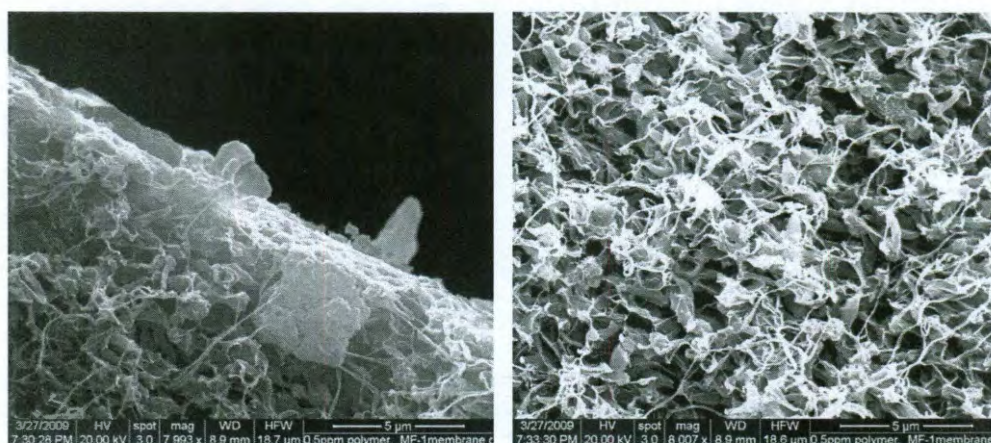
SEM analysis of the clean and fouled membranes revealed that surface pore blockage was the predominant fouling mechanism. The top and cross-sectional views of the MF-1 membranes fouled by 0.1 mg/L pDADMAC are presented in Figure 4-10 together with the clean membranes. pDADMAC formed large aggregates on the membrane surface, and these aggregates blocked openings of the membrane pores, leading to a reduction in membrane surface porosity. Careful inspection of the cross-sectional images (e.g., Figure 4-9 (f)) did not indicate any noticeable internal fouling (i.e., accumulation of foulants inside membrane pores), suggesting that pore constriction was not an important mechanism. Fouling of MF-2 and MF-3 was similar as shown in Figure 4-11 to 4-12. Similar phenomena were also observed with PACA and PAM (data not shown).





(a)

(b)



(c)

(d)

Figure 4-10 Cross sectional SEM images of clean (a, b) and fouled (c, d) MF-1 membrane (by 400-500 kDa pDADMAC)



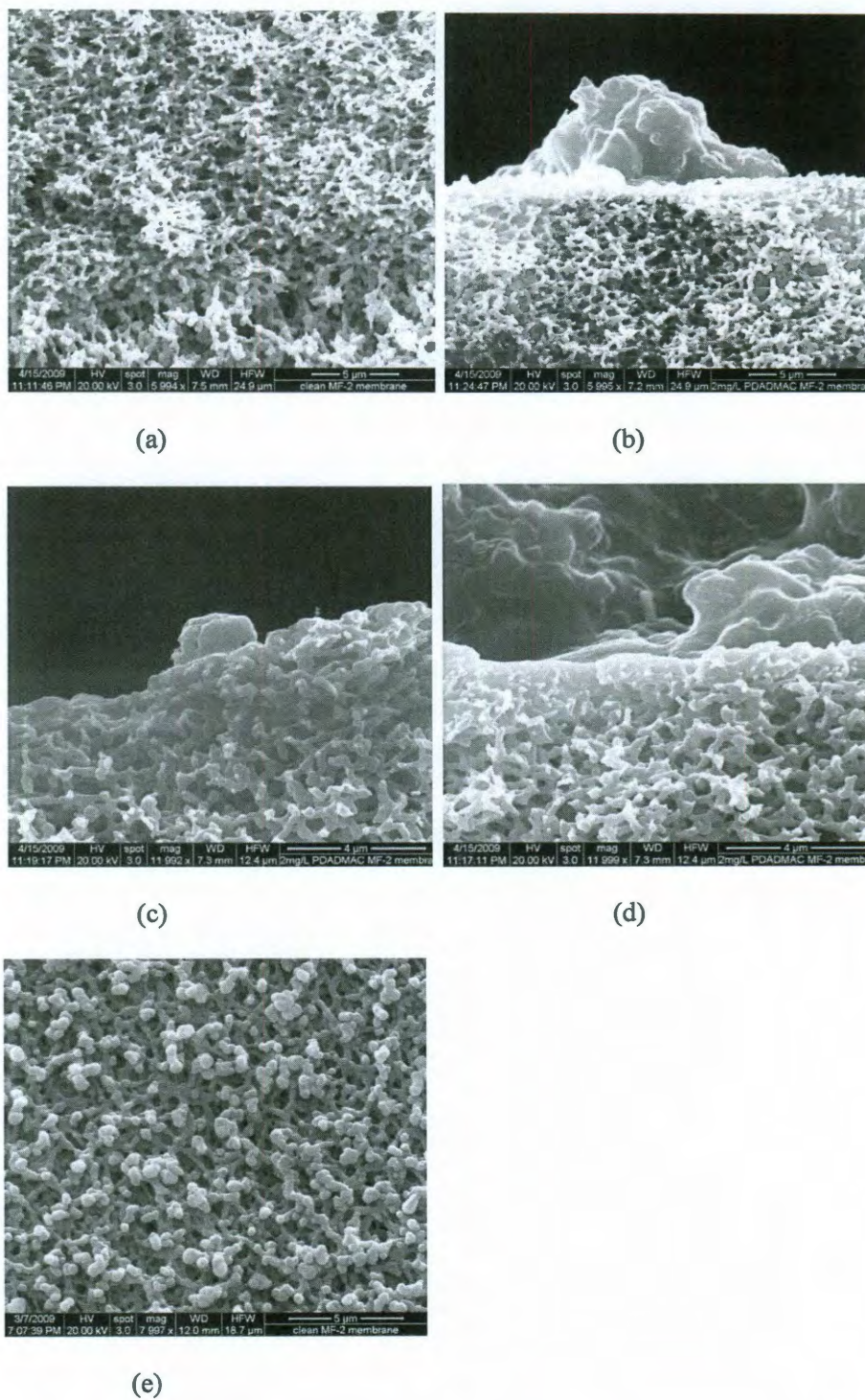


Figure 4-11 Cross sectional SEM images of clean (a, e) and fouled (b, c, d) MF-2 membrane (by 400-500 kDa pDADMAC)

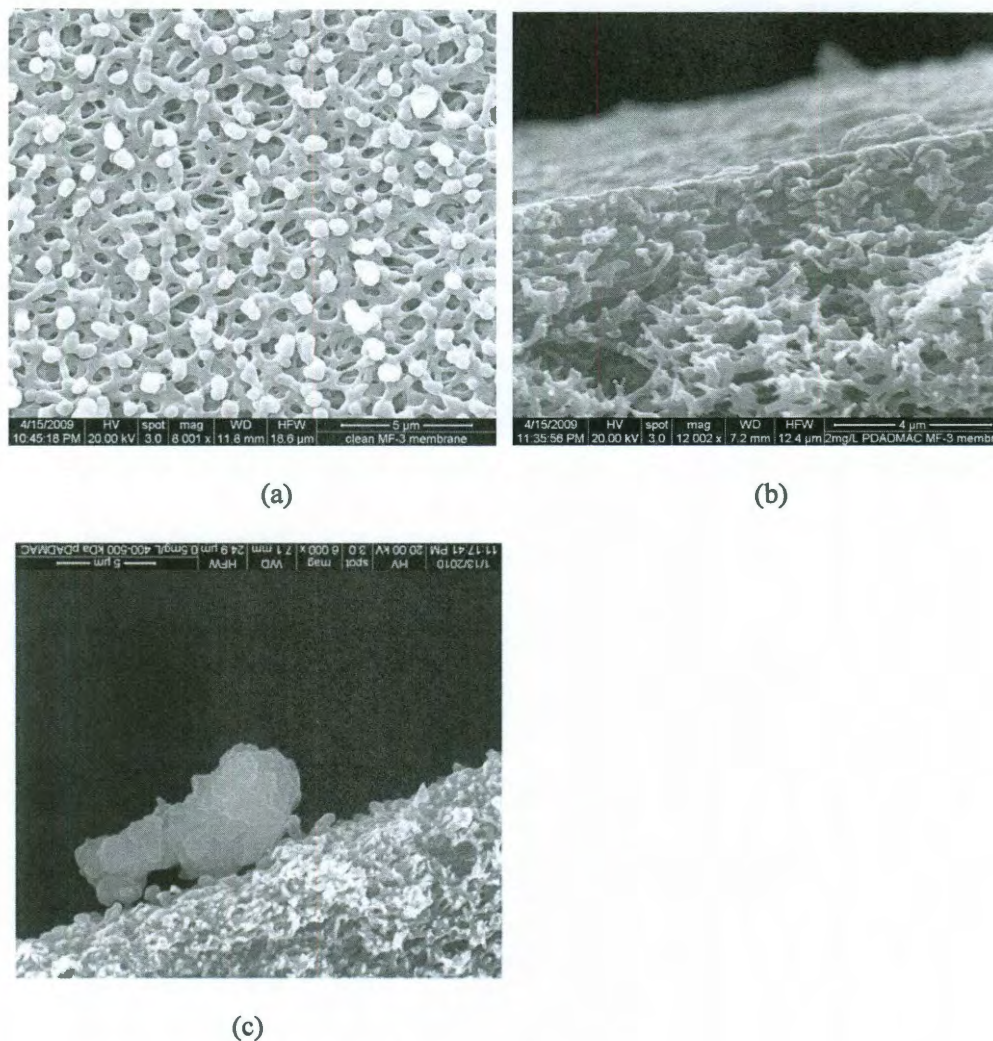


Figure 4-12 SEM images of clean (a) and fouled (b, c) MF-3 membrane (by 400-500 kDa pDADMAC)

Since the permeate flow is laminar, the flux can be approximated using the Hagen Poiseuille equation (Eq. 4-1), according to which the normalized TMP,  $\Delta P / \Delta P_0$ , is related to the changes in membrane porosity (Eq. 4-2).

$$J = \frac{\varepsilon r^2 \Delta P}{8\eta \Delta x} \quad \text{Eq. (4-1)}$$

$$\frac{\Delta P}{\Delta P_0} = \frac{\varepsilon_0}{\varepsilon} \quad \text{Eq. (4-2)}$$

where  $\Delta P_0$  and  $\Delta P$  are initial and final TMP,  $\varepsilon_0$  and  $\varepsilon$  surface porosity of clean and fouled membranes,  $r$  is the membrane pore radius and  $\Delta x$  is the effective pore length.

Table 4-2 Surface porosity of Clean and Fouled Membranes\*

Parameters	MF-1	MF-2	MF-3
$\varepsilon_0$	31.2±0.9	29.6±4.7	19.6±2.0
$\varepsilon$	18.7±2.9	15.5±1.5	12.3±1.3
$\varepsilon_0 / \varepsilon$	1.7	1.9	1.6
$\Delta P / \Delta P_0$	2.2	2.7	1.4

\* The feed solution contained 10 mM NaCl, and 0.1mg/L

400-500kDa pDADMAC at pH 7

Table 4-2 presents the membrane surface porosity before and after fouling by the 400-500 kDa pDADMAC measured by SEM imaging. The measured porosity change of MF-3 agrees well with the observed TMP increase, confirming that blockage of the pore opening is the main fouling mechanism. The measured porosity changes of the MF-1 and MF-2 membranes, however, predict lower TMP increase than that observed experimentally. This can be partially attributed to artifacts from image processing due to the highly heterogeneous surface of the MF-1 and MF-2 membranes, which makes

defining membrane pores difficult. With such artifacts, the possibility of intermediate blocking cannot be excluded.

The measured molecular size distributions of the polymers in Figure 4-3 suggest that the majority of the polymer molecules exist as individual molecules or small aggregates even at a concentration of 1 g/L, much smaller than the aggregates found in the SEM images. Therefore, it is speculated that the aggregates observed in the SEM images were formed on the membrane surface instead of in the bulk solution. This is supported by an approximate calculation of the foulant mass using the measured aggregate size and surface porosity, which suggests that the aggregates found on the membrane surface accounts for almost all the polymers in the feed solution. It is hypothesized that the polymer molecules and the small aggregates formed in the bulk solution preferably adsorb or deposit on the opening of small pores. They subsequently act as nuclei to catalyze formation of larger aggregates on the membrane surface as filtration proceeds. This hypothesis is supported by the observed changes in MF-1 membrane pore size distribution after fouling (Figure 4-13). As shown in Figure 4-13, after fouling by the 400-500 kDa pDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM, the pore size distribution of MF-1 shifted towards the larger pore size range, indicating that the smaller pores were preferentially blocked during filtration.



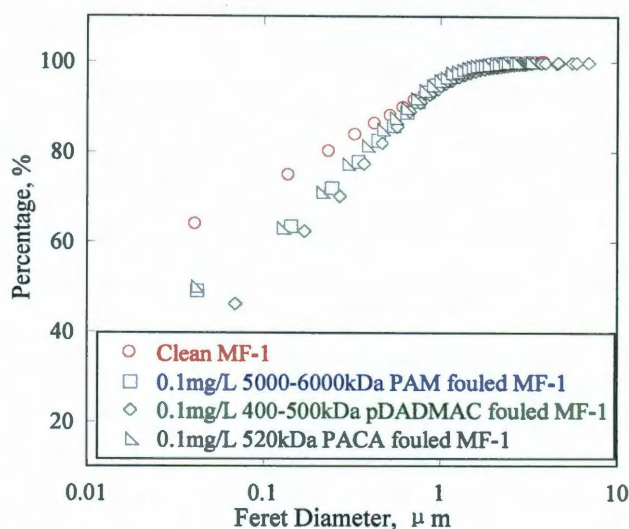


Figure 4-13 Pore size distribution of clean and fouled MF-1 membranes. The feed solution had a pH of 7 and contained 10mM NaCl. Feret diameter is the longest distance between any two points along the pore opening circle.

#### 4.4. Conclusions

This study demonstrates that carry-over of polymers used in the coagulation/flocculation pretreatment can cause severe fouling of MF membranes even at very low concentrations. MF membrane fouling by polymers strongly depends on the molecular weight, charge, and concentration of the polymer, as well as the membrane surface properties. Cationic polymers tend to cause greater fouling than anionic and nonionic polymers in synthetic feed water due to the strong electrostatic attraction between the positively charged polymer and the negatively charged membrane surface. Among polymers of the same charge, those with higher molecule weight have greater fouling potential. Although changes in electrostatic interaction due to changes in either

pH or calcium concentration did not have much impact on MF fouling, pH or calcium concentration can affect fouling by mediating specific foulant-foulant or foulant-membrane interactions. In spite of the small size of the polymers relative to the size of MF membrane pores, surface pore blockage was found to be the predominant fouling mechanism. Formation of large aggregates on the membrane surface suggests that prediction of fouling mechanisms based on foulant molecular size and membrane pore size can be erroneous sometimes. Membrane surface chemical and physical heterogeneity and specific membrane-foulant interactions may be more important than the physical screening mechanism.

***Chapter 5 Impact of Polymer Flocculants on  
Microfiltration of Surface Water—Part I:  
Coagulation Pretreatment<sup>2</sup>***

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<sup>2</sup> Manuscript prepared for submission to Water Research

## 5.1. Introduction

Coagulation using hydrolyzed metal salts is commonly used as a pretreatment for microfiltration of surface water in both new MF installations and retrofits of conventional treatment plants to increase removal of natural organic matter (NOM) and turbidity, reduce disinfection byproducts (DBPs) formation potential, and control membrane fouling (Farahbakhsh et al., 2004, Huang et al., 2009). In many coagulation-microfiltration systems, polymers are also applied in conjunction with the hydrolyzed metal salt as flocculants or coagulation aids. However, the role of polymer flocculants on the performance of the integrated coagulation/microfiltration processes, both in terms of treated water quality and membrane fouling, is largely unknown.

Polymer flocculants play an important role in controlling the size, structure and hence strength of floc particles. They are believed to increase floc size and strength and hence improve particle removal by sedimentation. Bridging, the mechanism in which particles attach to segments of polymer molecules adsorbed on other particles, is usually considered more effective to induce flocculation than charge neutralization. Therefore, molecular properties (e.g., sign of charge, charge density, molecular weight and molecular structure) that maximize bridging usually lead to larger and stronger flocs (Bolton and Gregory, 2007). With similar molecular weight, polymer flocculants of medium charge density results in the most particulate removal than polymer flocculants of high and low or none charge density. Because polymer flocculants of high charge density commonly induce electrostatic patch flocculation and polymer flocculants of medium charge normally brings bridging flocculation, which produces stronger bonding

between polymers and particulates. On the other hand, low or none charge density polymer flocculants tend to assume a coiled conformation, therefore, low or none charge density polymer flocculants have lower bonding capacity than polymer flocculants of medium charge density (Gill and Herrington, 1988, Gray and Ritchie, 2006, Smithpalmer et al., 1994) When the charge densities are the same, polymer flocculants of larger molecular weights produced larger flocs (Gill and Herrington, 1988) . With similar molecular weights, branched polymer produced larger and stronger flocs than linear polymer in a coagulation of kaolin suspension (Mpofu et al., 2003).

Removal of NOM is important because NOM is the primary DBP precursor and a major membrane foulant. NOM removal by coagulation using hydrolyzing metal salts is achieved through complexation, charge neutralization, and adsorption (Lee et al., 2003a, Yan et al., 2008a). Few studies have been done on the impact of polymer flocculants on removal of NOM using hydrolyzing metal salt as primary coagulant. While some studies reported increase in dissolved organic carbon (DOC) (Bolto et al., 2001, Jarvis et al., 2008b), others showed little or no additional DOC removal by polymer flocculants (Chang et al., 2005, Jarvis et al., 2008a). It is also unclear which fraction of NOM is affected by different polymer flocculants.

Floc size and structure is another important factor in MF membrane fouling. In direct filtration, it direct determines the cake layer structure and hence the hydraulic resistance; when sedimentation is used before MF, it determines the concentration and size distribution of residual particles after sedimentation. Despite the general belief that the use of polymer flocculants increase floc size and strength, reported observations under conditions optimized for NOM removal are not consistent. Jarvis et al. (Jarvis et

al., 2006) found that under optimum conditions cationic poly diallyldimethylammonium chloride (pDADMAC) reduced floc size and fractal dimension in coagulation of a high DOC and low alkalinity surface water using ferric sulfate, but a high molecular weight nonionic polyacrylamide was found to increase floc size while reducing fractal dimension of the large flocs formed (Jarvis et al., 2008b).

As part of a series of two studies aimed at assessing the role of commonly used polymer flocculants in microfiltration treatment of surface water, this paper reports the effects of three different types of polymer flocculants on the coagulation/flocculation pretreatment of two surface waters with respect to floc properties and NOM removal, two important factors affecting the performance of the down-stream MF process. To our knowledge, this is the first systematical study on the impact of polymer flocculants on the performance of coagulation-microfiltration processes. The results reveal that polymer flocculants have no impact on turbidity removal during coagulation/microfiltration. Polymer flocculants help remove DOC with high DOC water, only cationic polymers are able to remove additional  $UV_{254}$ , but different polymer flocculants remove different fraction of NOM. All the polymers are able to increase floc size and decrease fractal dimension.

## 5.2. Materials and Methods

### 5.2.1. Surface Waters

Two surface waters with notably different water quality were selected for this study. A low turbidity, low DOC water was collected from the Grand Lake at the intake of the Vinita Water Treatment Plant, Vinita, OK, and a medium turbidity, high DOC water was collected on April 28, 2009 from the Mississippi River at the intake of the Minneapolis Water Works, Minneapolis, MN. Water samples were shipped to the laboratory in high-density polyethylene (HDPE) containers immediately after collection and stored in dark at 4 °C until use. Basic water quality parameters of the two waters are summarized in Table 5-1. Experiments with each water were finished within one month after collection of the water samples. DOC and UV<sub>254</sub> were routinely monitored during this period, and no detectable water quality deterioration was found.

Table 5-1 Important water quality parameters of the two surface waters

Parameters	Surface water source	
	Mississippi River	Grand Lake
DOC ,(mg/L)	10.8±0.8	3.6±0.4
Alkalinity,(mg/L as CaCO <sub>3</sub> )	120.0±0.7	108.6±1.1
pH	8.14±0.09	8.06±0.05
Turbidity, (NTU)	9.0±1.0	2.2±0.1
UV <sub>254</sub> absorbance, cm <sup>-1</sup>	0.323±0.004	0.128±0.003

### 5.2.2. Primary Coagulant and Polymer Flocculants

Polyaluminum chloride (PACl) (Southern Water Consultants, Decatur, AL) was used as the primary coagulant. The PACl contains 15.8% (w/w)  $\text{Al}_2\text{O}_3$  with a 71.5% basicity. Three types of analytical grade polymer flocculants of different molecular charges were purchased from Sigma Aldrich (St. Louis, MO): poly (diallyldimethylammonium) chloride (pDADMAC) of 100 - 200 and 400 - 500 kDa, poly (acrylic acid-co-acrylamide) (PACA) of 200 and 520 kDa, and polyacrylamide (PAM) of 5000 - 6000 kDa. The 200 kDa PACA and the 520 kDa PACA contain 80% and 20% acrylic acid monomer units respectively. Electrophoretic mobility and hydrodynamic radius of each polymer were determined by phase analysis light scattering (PALS) and dynamic light scattering (DLS) respectively using a Zen3600 Zetasizer Nano (Malvern Ltd., Malvern, UK). Details of the characterization methods and results can be found in a previous publication (Wang et al., 2011).

### 5.2.3. Coagulation/Flocculation Experiments

Coagulation/flocculation experiments were performed at 22 °C in a standard jar test apparatus (Phillips & Bird). Two minutes of rapid mixing at 100 rpm was followed by slow mixing at 30 rpm for 20 min, after which mixing was stopped for sedimentation. PACl was added at the onset of the rapid mixing, and a polymer flocculant was added 30 seconds afterwards. PACl doses ranging from 0 to 30 mg/L as  $\text{Al}_2\text{O}_3$  were applied in conjunction with 0.5 to 5 mg/L of each polymer flocculant. Samples were collected from the supernatant after 30 (for Grant Lake water) or 60 min (for Mississippi River water) of



sedimentation time and filtered through 0.2  $\mu\text{m}$  (absolute rating) polyvinylidene fluoride (PVDF) membranes (Pall Corporation, Port Washington, NY) housed in syringe filters. The PVDF membrane used was the same as the flat sheet membrane used in the subsequent microfiltration experiments reported in Part II of this study (Wang et al., 2011). The first 5 mL of each filtrate sample was discarded to saturate the NOM adsorption capacity of the membrane. The filtered samples were then analyzed for turbidity, dissolved organic carbon (DOC) concentration,  $\text{UV}_{254}$  absorbance, and NOM molecular weight distribution. For NOM molecular weight distribution analysis, a low protein binding regenerated cellulose (RC) membrane (Corning incorporated, Corning, NY) was also used to minimize NOM adsorption on the membrane.

Turbidity was measured using a 2100N Turbidimeter (Hach, Loveland, Colorado). DOC concentration and UV absorbance at 254 nm were used to assess NOM removal and were measured using a high sensitivity total organic carbon analyzer (TOC-V<sub>CSH</sub>, Shimadzu Scientific Instruments, Kyoto, Japan) and an UV-Vis spectrophotometer (Ultrospec 2100 Pro, Shimadzu Scientific Instruments, Kyoto, Japan) respectively. NOM molecular weight (MW) distribution was analyzed by size exclusion chromatography (SEC) using a high performance liquid chromatography (HPLC) system (Waters 2690, Waters Co., Milford, MA) equipped with a Protein-Pak<sup>TM</sup> 125 column and a UV detector (Waters Co., Milford, MA) following a previously published protocol (Huang et al., 2008, Li et al., 2003, Pelekani et al., 1999). Polystyrene sulfonate of 35, 18, 4.6, and 1.8 kDa (Polysciences Inc., Warrington, PA) and acetone (58 Da) (Fisher Scientific, Fair Lawn, NJ) were used as calibration standards. The mobile phase was a 0.02 M phosphate buffer at pH 6.8 with the total ionic strength adjusted to 0.1 M using NaCl. The flow rate

used was 1 mL/min. The UV absorbance of the samples was monitored at 254 nm. It is noted that none of the polymer flocculants used in this study absorbs UV and hence does not interfere with the SEC analysis.

#### 5.2.4. Measurement of Floc Size and Fractal Dimension

Coagulation/flocculation experiments were also performed for real time analysis of floc size and fractal dimension by static light scattering and small angle light scattering (Jarvis et al., 2008b), respectively, using a Malvern Mastersizer 2000 instrument (Malvern, UK). Instead of using the built-in pump of the instrument, the coagulated water was drawn continuously through the measurement cell of the Mastersizer by a Filtertec peristaltic pump (SciLog, Middleton, WI) installed downstream of the measurement cell in order to avoid floc breakage. An optimum pumping rate of 20 mL/min was found to prevent floc breakage and sedimentation during the measurement. The slow mixing time in coagulation/flocculation experiments was extended to 25 min to allow multiple measurements at around 20 min. At least 7 measurements were made between 18 and 22 min during slow mixing.

The floc fractal dimension ( $D_f$ ) was determined by linear regression of the scattered light intensity ( $I$ ) as a function of the difference in the magnitude between the incident and scattered light ( $Q$ ) (Equations 4-3 and 4-4).

$$I(Q) \propto Q^{-D_f} \quad \text{Eq. 4-3}$$

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad \text{Eq. 4-4}$$

Here,  $n$  is the refractive index of the suspending medium (i.e., water),  $\theta$  is the angle of light scattering ( $0.01$ - $40.6^\circ$ ), and  $\lambda$  is the wavelength of the radiation in vacuum ( $633$  nm).

## 5.3. Results and discussion

### 5.3.1. Effect of polymer flocculants on turbidity removal

Turbidity is an important water quality parameter. In this study, the impact of polymer flocculants on turbidity removal was evaluated using the Grand Lake water and three polymer flocculants:  $400$ - $500$  kDa pDADMAC,  $520$  kDa PACA, and  $5000$ - $6000$  kDa PAM. The turbidity was measured after coagulation, sedimentation, and microfiltration with  $0.2$   $\mu\text{m}$  PVDF membranes. The results are presented in Figure 5-1. As shown in Figure 5-1 (a), the turbidity of the clarified water decreased with increasing PACl dosage from  $0.83$  to less than  $0.2$  NTU after  $30$  min of sedimentation. The turbidity was significantly lower ( $0.09$  to  $0.15$  NTU) after filtration by the PVDF membrane and was relatively independent of PACl dosage. None of the polymer flocculants tested was found to improve turbidity removal.

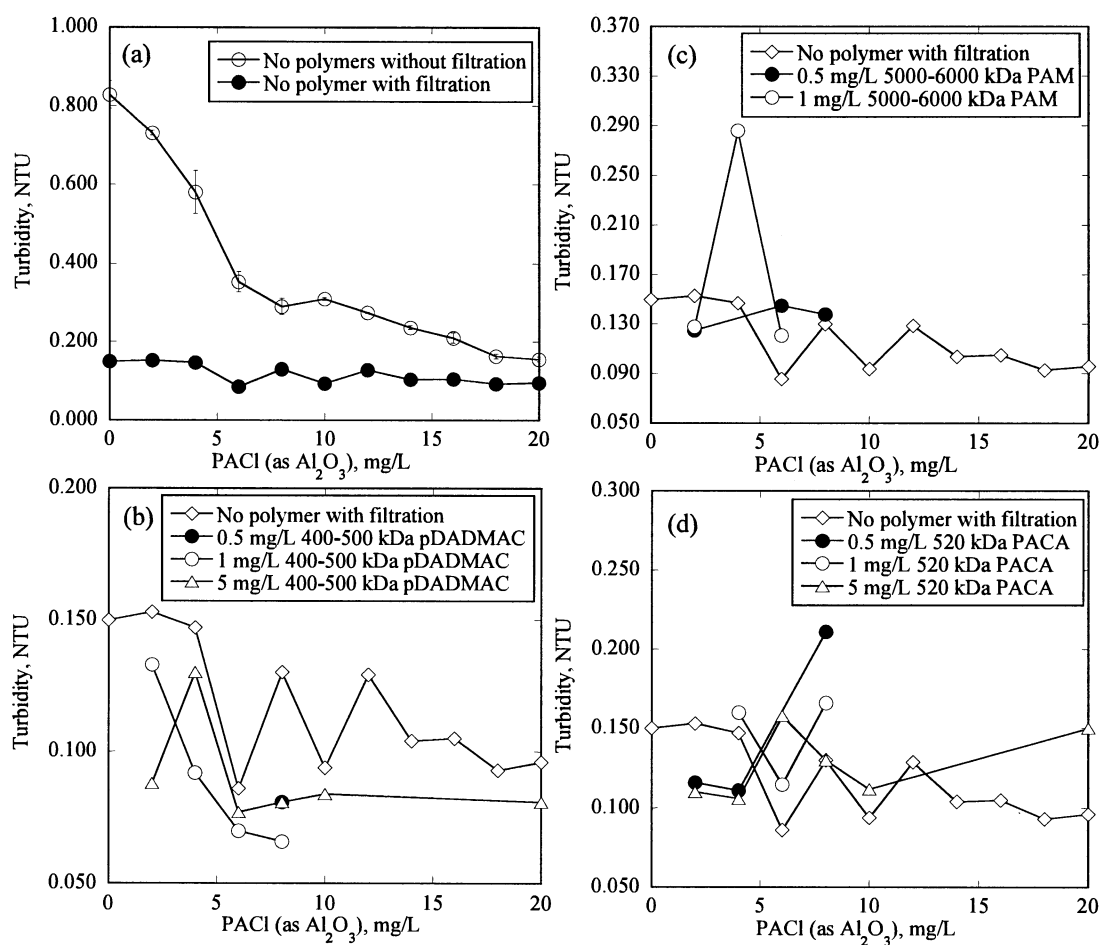


Figure 5-1 Impact of polymer flocculants on turbidity removal after coagulation, sedimentation (30min), and filtration with 0.2  $\mu\text{m}$  PVDF membranes: (a) PACl only; (b) PACl with 400-500 kDa pDADMAC; (c) PACl with 5000-6000 kDa PAM; (d) PACl with 520 kDa PACA .

### 5.3.2. Effect of Polymer Flocculants on NOM Removal

#### 5.3.2.1. Mississippi River Water

Figures 5-2 to 5-4 present the DOC and UV254 removal from the Mississippi River water after coagulation/flocculation, sedimentation and PVDF membrane filtration. As expected, both DOC and UV254 decreased with increasing PACl dosage in the absence of the polymer flocculant. The prehydrolyzed PACl mainly contains monomeric, moderately hydrolyzed (e.g.,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ), and colloidal ( $\text{Al}(\text{OH})_3$ ) aluminum species (Wang et al., 2004), which remove NOM by complexation, charge neutralization, and adsorption respectively (Yan et al., 2008a). At the highest PACl dosage tested (25 mg/L as  $\text{Al}_2\text{O}_3$ ), 48.7 and 77.6% removal were achieved for DOC and UV254, respectively. Removal of UV254 was found to be consistently higher than DOC removal. This is because UV254 absorbing NOM are usually large, hydrophobic molecules with charge densities an order of magnitude higher than hydrophilic NOM and are preferably removed by coagulation (Sharp et al., 2006a, Sharp et al., 2004).

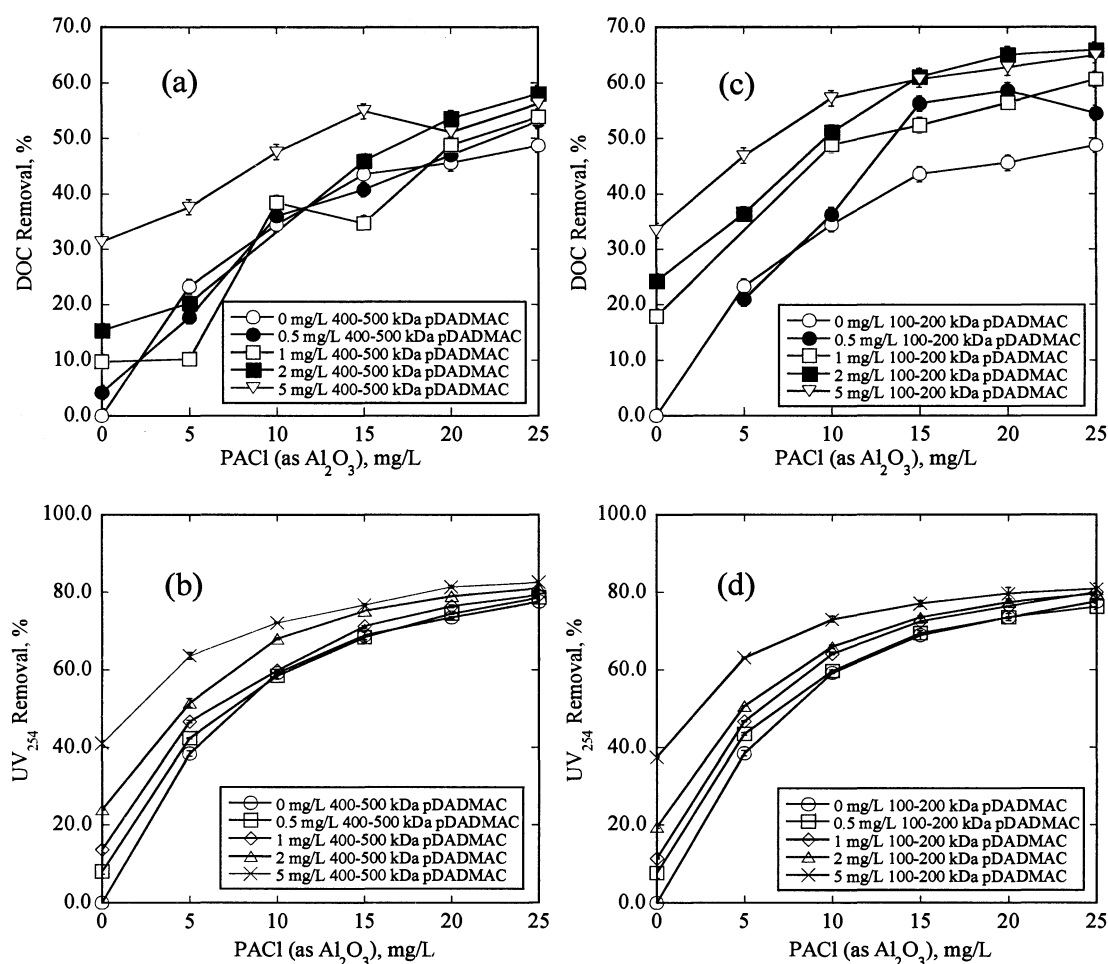


Figure 5-2 DOM removal of Mississippi River water using PACl plus 400-500 kDa pDADMAC ((a) DOC, (b) UV<sub>254</sub>) and 100-200 kDa pDADMAC ((c) DOC, (d) UV<sub>254</sub>). The sedimentation time was 60 min.

Use of pDADMAC alone resulted in notable removal of DOC and UV<sub>254</sub>. This is consistent with previous studies that used pDADMAC as the primary coagulant for NOM removal (Lee and Westerhoff, 2006). The removal is attributed to adsorption of negatively charged NOM to positively charge pDADMAC and subsequent charge neutralization, which leads to coagulation. When used in conjunction of PACl, the two

pDADMAC polymers enhanced both DOC and  $UV_{254}$  removal at all PACl dosages, and DOC and  $UV_{254}$  removal increased with increasing pDADMAC concentration. The addition of 5 mg/L 100-200 kDa pDADMAC increased DOC removal to 64.8% at a PACl dosage of 25 mg/L as  $Al_2O_3$ . The effect of pDADMAC on DOC removal was relatively independent of the PACl dosage, while its effect on  $UV_{254}$  removal decreased with increasing PACl concentration, similar to that reported in a previous study (Lee and Westerhoff, 2006). This suggests that pDADMAC increased removal of non-UV absorbing NOM at high PACl doses. is likely because high dosage PACl already removed a significant portion of  $UV_{254}$ ; meanwhile, more free pDADMAC molecules might be incorporated into PACl flocs and reduced the effect of pDADMAC on  $UV_{254}$  removal.

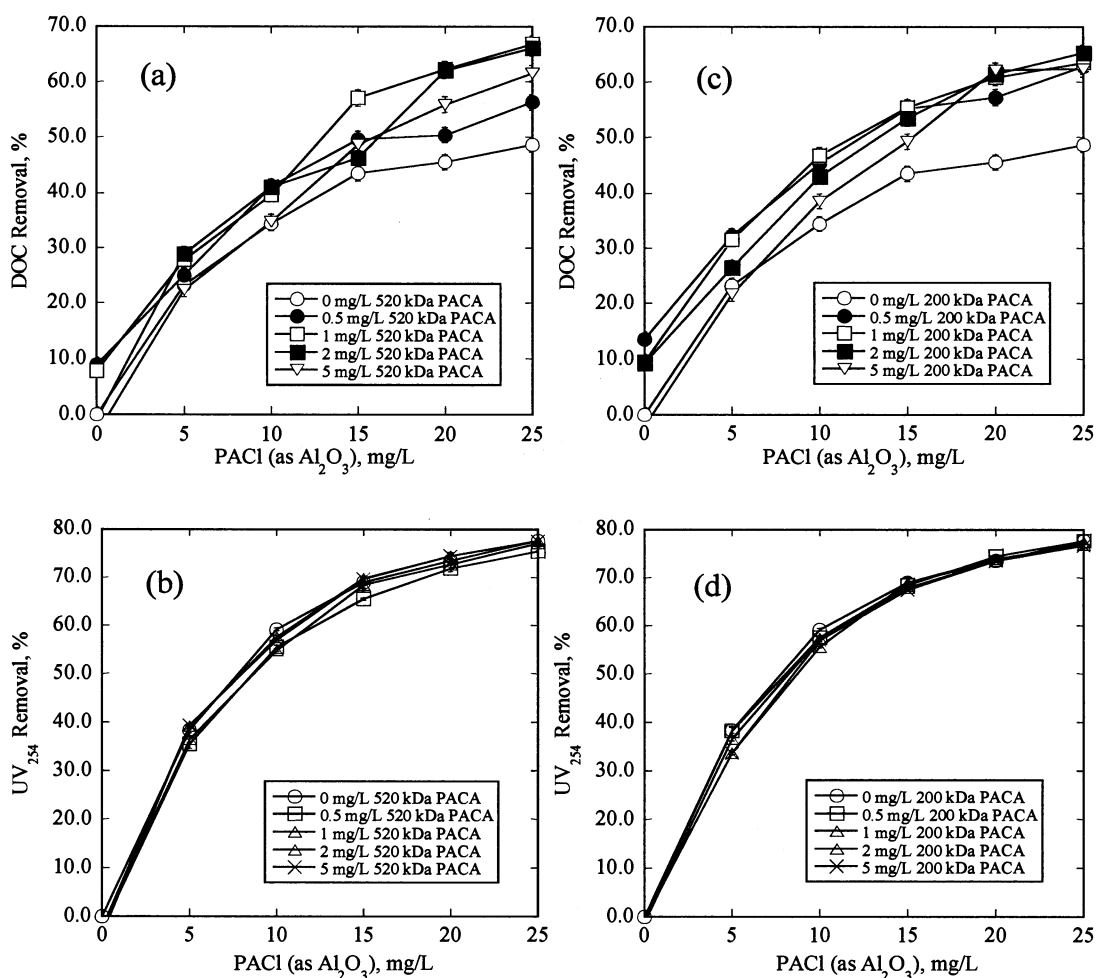


Figure 5-3 DOM removal of Mississippi River water using PACl plus 520 kDa PACA ((a) DOC, (b) UV<sub>254</sub>) and 200 kDa PACA ((c) DOC, (d) UV<sub>254</sub>) respectively. The sedimentation time was 60 min.

The anionic PACA and the non-ionic PAM also improved DOC removal (Figure 5-3 and 5-4). However, their effects are clearly different from that of pDADMAC. For both PACA and PAM, DOC removal increased when the polymer concentration increased from 0 to 1 mg/L, after which DOC removal decreased with increasing polymer



concentration. Neither PACA nor PAM had any impact on  $UV_{254}$ . These results suggest that unlike the cationic pDADMAC, which acts as a coagulant, PACA and PAM function as flocculants what cause aggregation of aluminum floc with adsorbed NOM. When overdosed, a fraction of PACA or PAC molecules are not incorporated into the floc particles; residual PACA or PAM in the clarified water is partly responsible for the observed increase in DOC concentration. Indeed, at 5 mg/L PACA, the clarified water showed higher DOC (11.1 mg/L) than the untreated water. In addition, PACA and PAM can compete with the UV absorbing, hydrophobic NOM for adsorption sites on floc particles. The net result of increased floc size and hence better sedimentation, and the reduced adsorption of hydrophobic NOM is unchanged  $UV_{254}$  removal. The competition as well as residual polymer decreases at higher PACl doses, when more adsorption sites are available. Therefore, polymer addition provided better DOC removal at higher PACl doses.

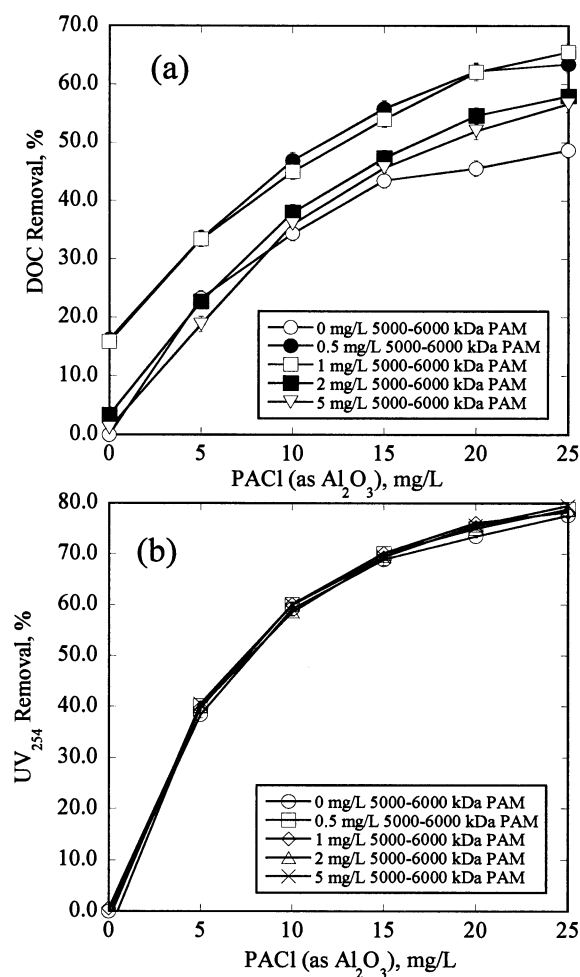


Figure 5-4 DOM removal for Mississippi River water using PACl plus 5000-6000 kDa PAM ((a) DOC and (b)  $\text{UV}_{254}$ ). The sedimentation time was 60 min.

### 5.3.2.2. Grand Lake Water

Figure 5-5 shows DOC removal from the Grande Lake Water after coagulation/flocculation, sedimentation and PVDF membrane filtration. Unlike that observed with the Mississippi River water, the two pDADMACs only slightly increased

DOC removal at low concentrations at 0.5 and 1 mg/L when the PACl dosage was low. At the highest pDADMAC concentration tested, 5mg/L, the DOC of the clarified water became significantly higher than that of the raw water, suggesting a large fraction of pDADMAC was not incorporated in the floc. This is consistent with the low DOC concentration of the Grand Lake water, which provides fewer negatively charged sites for pDADMAC to adsorb to. The 100-200 kDa pDADMAC, at 5 mg/L, caused significantly greater reduction in DOC than the 400-500 kDa pDADMAC, suggesting less adsorption of lower molecular weight polymers when the charge density is the same.

The negatively charged PACAs and neutral PAM had little effect on DOC removal when the polymer dosage was low, suggesting no significant flocculation due to the addition of the polymer. This is consistent with the negligible additional turbidity removal in the presence of PACA or PAM (Figure 5-1). When the PACA concentration increased above 0.5 mg/L, residual PACA led to increase in clarified DOC. PAM was not able to enhance flocculation at 0.5 mg/L, as indicated by the decreased DOC removal (Figure 5-5(e)). At 1 mg/L, it slightly enhanced DOC removal at PACl dosages between 8 and 20 mg/L as  $\text{Al}_2\text{O}_3$ . These results, when compared to those obtained with the Mississippi River water, suggest that use of polymer flocculants offers minimal benefits in NOM removal from low DOC surface waters. When polymers are used, careful control of polymer flocculant dose is extremely important; overdosing, which could occur at concentrations as low as 1 mg/L, leads to significant residual polymer concentration in the clarified water and therefore severe fouling of the downstream membrane units(Wang et al., 2011).

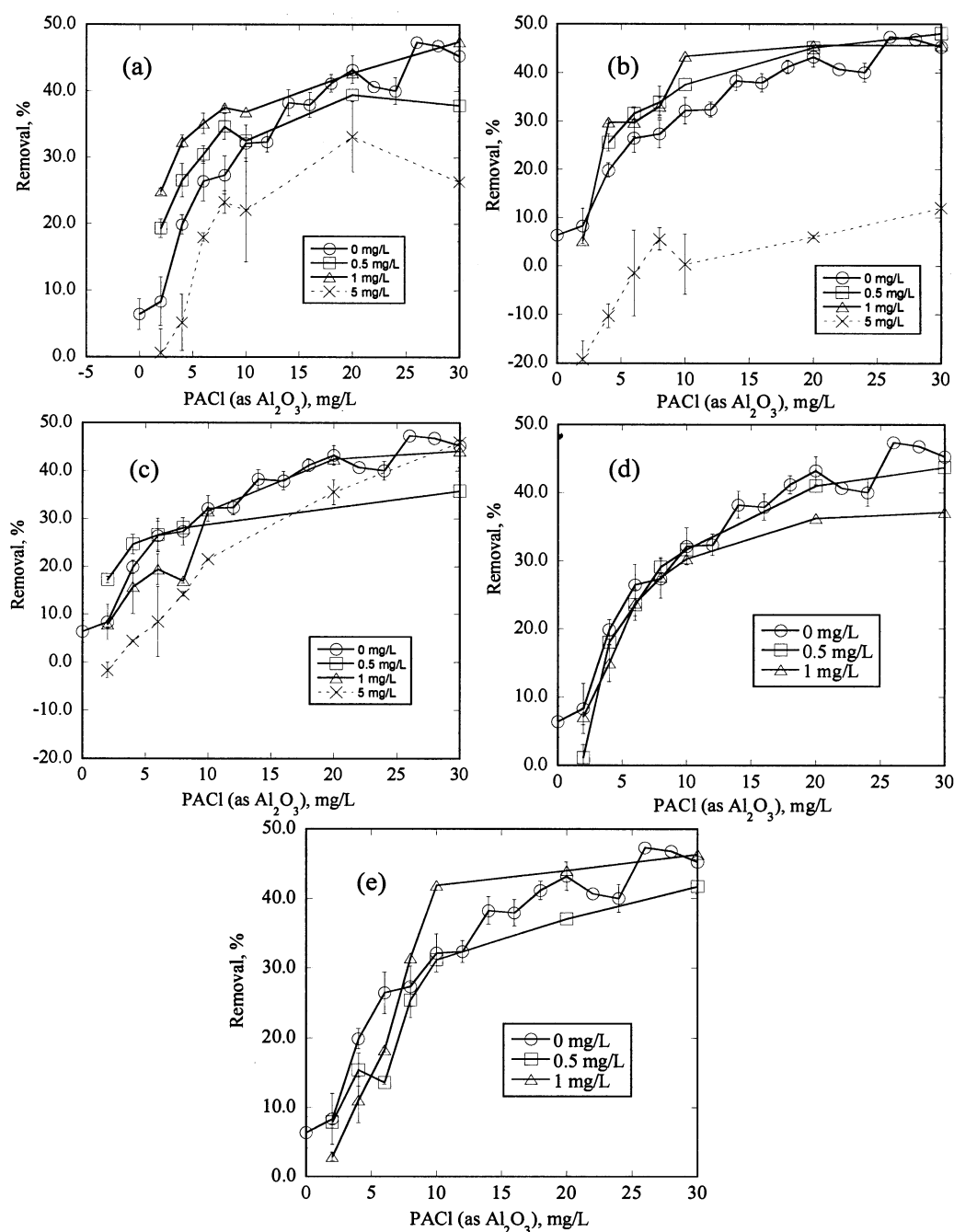


Figure 5-5 DOC removal from the Grand Lake water using PACl and 400-500 kDa pDADMAC (a), 100-200 kDa pDADMAC (b), 520 kDa PACA (c), 200 kDa PACA (d), and 5000-6000 kDa PAM (e). The sedimentation time was 30 min.

### 5.3.3. Effect of polymer flocculants on NOM composition

The impact of polymer flocculants on the composition of residual NOM was investigated by comparing the molecular weight distribution of NOM after coagulation/flocculation treatment with and without polymer flocculants. Considering that the PVDF membrane may adsorb some NOM even after the first 5 mL of filtrate, parallel analyses were done with low protein binding RC membranes. 10 mg/L PACl and 1 mg/L polymer flocculant were used for the Grand Lake water, while 15mg/L PACl and 1 mg/L polymer flocculant were used for the Mississippi River water. It should be borne in mind that since a UV detector was used for the SEC analysis, the molecular weight distributions presented here only represent the UV absorbing fraction of NOM.

A comparison of overall  $UV_{254}$  removal for the Mississippi river water between HPSEC and spectrophotometer methods is presented in Figure 5-6. The overall  $UV_{254}$  removals measured by HPSEC method were calculated by summing up the UV responses of all molecular weights for each polymer. Although the  $UV_{254}$  removals using the two methods do not match exactly with each other, the general trends are similar. The cationic polymers removed the most  $UV_{254}$ , the non-cationic removed some  $UV_{254}$  as well but less than cationic polymers. The discrepancy might possibly be attributed to the difference in calibration and operation between the two methods.

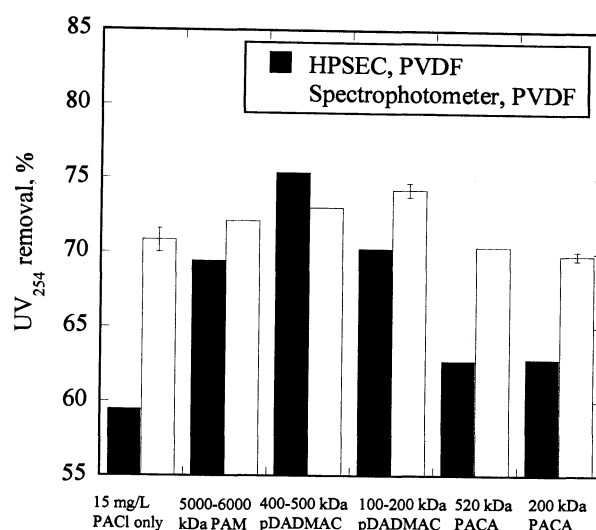


Figure 5-6 Comparison of  $UV_{254}$  absorbance after syringe filtration using PVDF and LPB membrane between HPSEC and spectrophotometer methods. The water used was Mississippi river water, and 15 mg/L PACl and 1 mg/L polymer flocculants were dosed for all the experiments

Figure 5-7 presents the results for the Mississippi River water (Figure 5-7a) and the Grand Lake water (Figure 5-7b) after RC membrane filtration. The raw Mississippi River water NOM has a molecular weight up to 9000 Da. The molecular weight distribution (MWD) from 0 to 4000 Da is shown in Figure 5-7. The higher MW fraction (4000 to 9000 Da) was completely removed after coagulation, sedimentation and membrane filtration. PACl alone removed a significant amount of NOM with MW above 4000 Da, but had no impact on smaller NOM. None of the polymers tested was able to remove these low MW NOM except for the two pDADMACs in the Grand Lake water, which removed a small amount of NOM below 3300 Da. In the higher MW range ( $> \sim 1500$  Da), PACA and PAM slightly improved NOM removal, while pDADMAC,

especially the higher molecular weight (400-500 kDa) showed significantly more removal. The greater NOM removal by the 400-500 kDa pDADMAC is attributed to more effective bridging (Gill and Herrington, 1988). These results show that polymer flocculants primarily enhance removal of large NOM molecules, similar to results obtained using polymers as the primary coagulant.

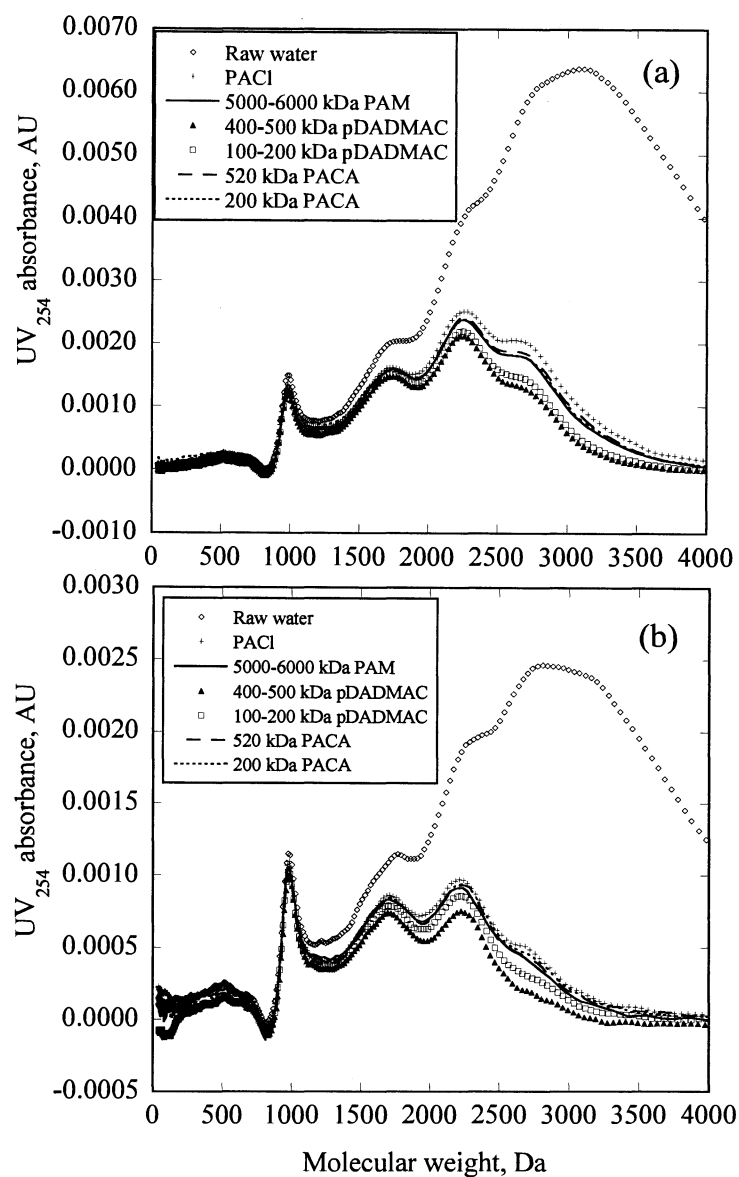


Figure 5-7 Residual NOM molecular weight distribution after filtration: (a) Mississippi river water with LPB membrane, 15 mg/L PACl plus 1 mg/L polymer flocculants were used, the sedimentation time was 60 min ; (b) Grand lake water with LPB membrane, 10 mg/L PACl plus 1 mg/L polymer flocculants were used, the sedimentation time was 30 min.



Similar phenomena as shown in Figure 5-8 were observed for the two waters with PVDF membrane. A comparison between filtration using PVDF and LPB membranes after HPSEC was first conducted. The comparison showed difference between the two membranes only for the 100-200 kDa pDADMAC, which is presented in Figure 5-9. The NOM MW distribution lines by using 100-200 kDa pDADMAC moved to lower positions compared to filtrations with LPB membrane especially for the Mississippi River water. But this is not observed with the 400-500 kDa pDADMAC as demonstrated in Figure 5-10. Since the only difference between the 100-200 kDa and 400-500 kDa pDADMACs is their size (see their similar electrophoretic mobility in our previous publication (Wang et al., 2010)), it is speculated that the smaller 100-200 kDa pDADMAC removes a different portion of the NOM from the 400-500 kDa pDADMAC, and the residual NOM portion by using 100-200 kDa pDADMAC is more easily retained by the PVDF membrane. The additionally removed NOM MW range by PVDF membrane extends to approximately 1100 to 4000 Da compared to the LPB membrane. Obviously, this extension is caused by the PVDF membrane itself, which means that the PVDF membrane is easier to be fouled by NOM.

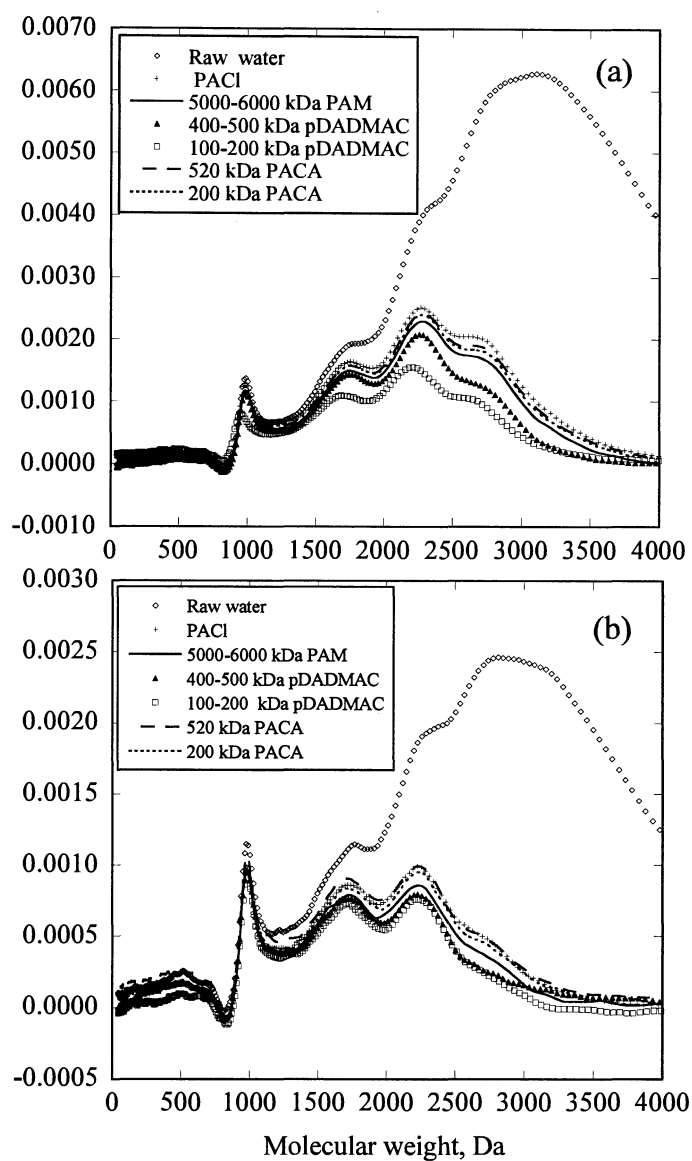


Figure 5-8 Residual NOM molecular weight distribution after PVDF membrane filtration:

(a) Mississippi river water; 15 mg/L PACl, 1 mg/L polymer flocculant, sedimentation

time = 60 min. (b) Grand Lake water; 10 mg/L PACl, 1 mg/L polymer flocculant,

sedimentation time = 30min.

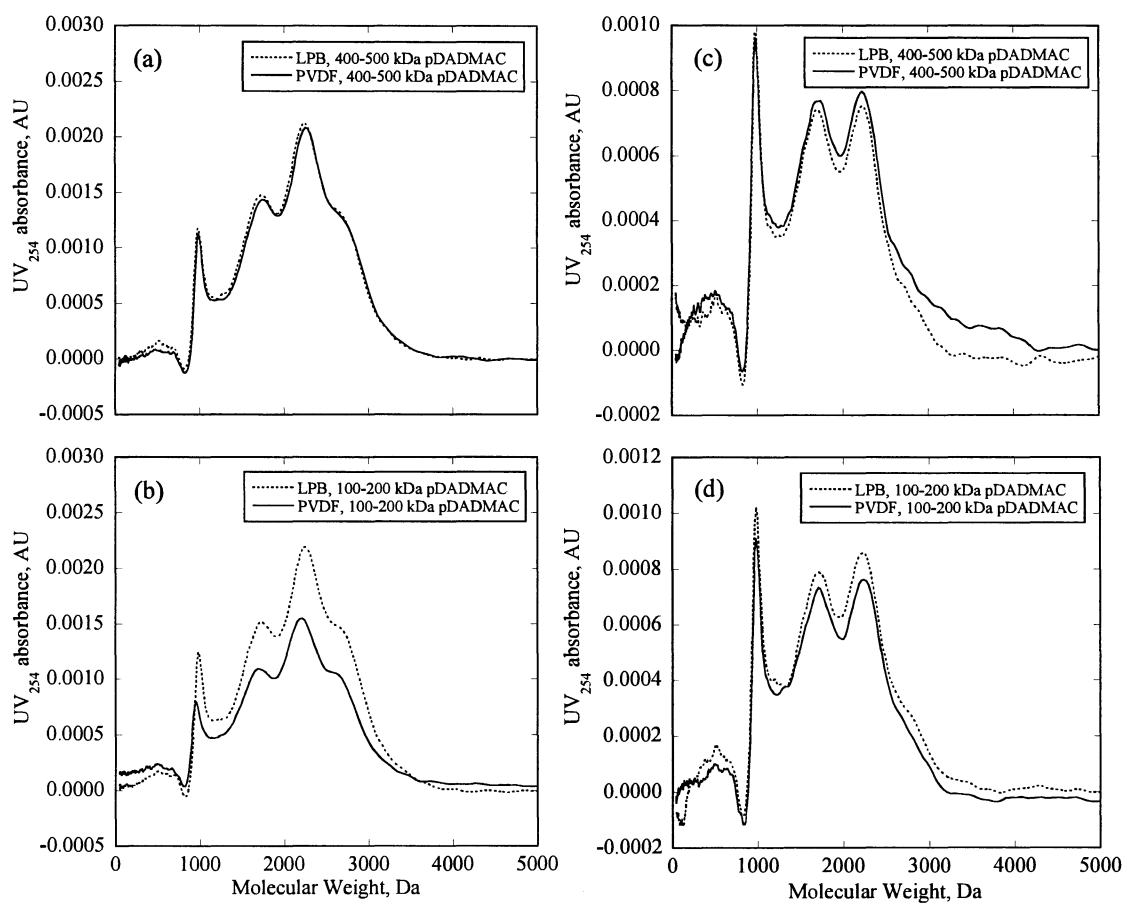


Figure 5-9 Comparisons of residual NOM molecular weight distributions of the Mississippi River water (a, b) and the Grand Lake water (c, d) between LPB and PVDF membranes.

#### 5.3.4. Effect of Polymer Flocculants on Floc Size and Structure

Floc properties such as size and structure are very important in determining their settling behavior and membrane fouling potential. In the direct filtration mode, cake formation is a major membrane fouling mechanism (Ho et al. 2000). The main factors that control the cake layer resistance are floc size and fractal dimension, and it has been suggested that flocs of smaller size and higher fractal dimension result in higher specific cake layer resistance (Lee et al., 2005b, Park et al., 2006a). In our study, the impact of polymer flocculants on floc properties was investigated using Mississippi River water and three polymer flocculants: 400-500 kDa PDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM. A range of PACl-to-polymer ratios were tested.

Figure 5-10 presents the size and fractal dimension of flocs formed in the Mississippi River water at the end of the 20 min flocculation. Each data point is the average of 7 measurements. In general, all polymers increased floc size, and the floc size increased with the increase of the polymer-to-PACl ratio. Addition of 1 mg/L of the anionic polymer PACA slightly reduced the floc size at the PACl dosage of 20 mg/L. Among the three polymers tested, addition of the 5000-6000 kDa PAM resulted in the greatest increase in floc size; the addition of 0.5 mg/L PAM increased the floc size from 298  $\mu\text{m}$  when 15 mg/L PACl was used alone to around 626  $\mu\text{m}$ . The sizes of flocs formed in the presence of the 520 kDa PACA and the 400-500 kDa pDADMAC were similar, with the 400-500 kDa pDADMAC generating the smallest floc particles. These results suggest that under the conditions tested in our study, polymer molecular weight is the most important factor in determining floc size; the differences observed among the

polymers are also consistent with the different flocculation mechanisms of the polymers: The high MW neutral PAM and negatively charged PACA flocculate through bridging while positively charged pDADMAC functions mainly through charge neutralization.

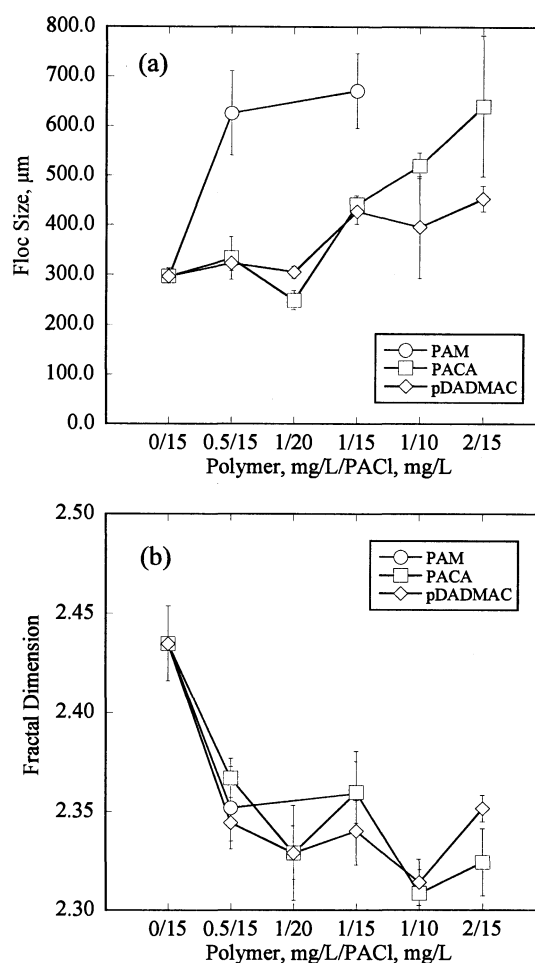


Figure 5-10 Floc size and fractal dimension at the end of 20 min flocculation

All the three polymers tested had similar effects on the floc fractal dimension. Figure 5-10(b) shows that the fractal dimension of the floc particles decreased with increasing polymer to PACl ratio, suggesting looser, more open structure of the floc particles. The fractal dimension is the lowest when the polymer/PACl ratio is 1/10. The

lowest fractal dimension at polymer/PACl ratio of 1/10 can be attributed to the lowest PACl concentration used and hence highest organic content and most open floc structure. A similar phenomenon was observed by Jarvis et al. (Jarvis et al., 2008b) during surface water flocculation using neutral PAM; the highest PAM dosage led to the smallest maximum floc fractal dimension.

## 5.4. Conclusions

Our study investigated effects of polymer flocculants with different molecular characteristics on the coagulation pretreatment of surface waters of different qualities. None of the polymer flocculants used evidently increased turbidity removal when microfiltration was used. The impact of polymer flocculants on NOM removal strongly depends on the water quality and the molecular characteristics of the polymer. For low DOC waters, none of the polymer flocculants tested was able to improve NOM removal; over-dosage of the polymer actually led to increase in DOC concentration due to significant residual of the polymer in filtered water. Some improvement in NOM removal was found for a high DOC water, but different polymers seem to remove different NOM fractions. Only the cationic pDADMACs removed UV absorbing NOM, likely through charge neutralization. HPSEC Analyses show that residual NOM molecules after PACl coagulation are all in the low molecular weight range (<4000 Da). The cationic pDADMAC enhanced removal of NOM in MW range of 1100-4000 Da. The smaller NOM molecules were not affected. The use of polymer flocculants have a great impact on floc size and structure. Increasing the polymer/PACl ratio results in larger, looser and more open floc particles, which should bring about lower specific cake layer resistance

according to Lee et al. (2005) and Park et al. (2006). These findings suggest that the use of polymer flocculants, especially cationic polymers, has some benefit in treating high DOC surface waters of level; their use for low DOC waters, however, should be evaluated carefully. The connection between the impact of polymer flocculants on floc properties and the impact of floc properties on membrane fouling will be reported in our next publication.

***Chapter 6 Impact of Polymer Flocculants on  
Microfiltration of Surface Water—Part II:  
Membrane Filtration<sup>3</sup>***

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<sup>3</sup> Manuscript prepared for submission to Water Research



## 6.1. Introduction

Microfiltration (MF) is increasingly used for surface water treatment due to its small footprint, automatic control, and superior treated water quality. However, microfiltration alone is not able to effectively remove natural organic matter (NOM), which can potentially form carcinogenic disinfection by products (DBPs) during chemical disinfection. In addition, directly application of microfiltration to high turbidity water could lead to severe fouling of the MF membranes. Therefore, coagulation as the most successful pretreatment for microfiltration (Farahbakhsh et al., 2004, Huang et al., 2009), usually with hydrolyzed metal salts, is often applied before the MF process to improve NOM removal as well as to reduce membrane fouling. At the same time, polymer flocculants, which are commonly used in the conventional treatment process to enhance floc sedimentation, are adopted in the coagulation-microfiltration process by many drinking water treatment plants.

However, little is known about the impacts of polymer flocculants on the performance of coagulation-microfiltration systems. We report a two-part study on the role of polymer flocculants in coagulation-microfiltration treatment of surface water. The first part of our study evaluated the impact of polymer flocculants of different molecular characteristics on turbidity and NOM removal as well as on the size and structure of floc particles. The results showed that polymer flocculants could improve NOM removal from high DOC water, but had no or negative impact on permeate DOC for low DOC water. The polymer flocculants were also found to greatly increase floc particle size and fractal dimension.

Both NOM and suspended particles (e.g., floc after coagulation) are important membrane foulants. The relative importance of the two groups of foulants depends on the source water quality, the membrane characteristics, and the pretreatment process. Without pretreatment, small colloids of 3-20 nm in diameter have been proved to be the most important foulants, the colloidal foulants could include both organic and inorganic matter, but organic matter had the largest fraction (Howe and Clark, 2002). Lee et al. (Lee et al., 2004) found that surface water with greater hydrophilic fraction (e.g. polysaccharides) caused the most membrane fouling during their research, in which both hydrophilic and hydrophobic membranes were used. The polysaccharide-like matter organic matter was also reported to cause the irreversible fouling of microfiltration (MF) and ultrafiltration (UF) membrane (Kimura et al., 2004). It was proposed that hydrophobic (humic-like) matters first adsorbed on the membrane and narrowed the membrane pores, and then the hydrophilic compounds of larger size would plug the narrowed pores (Yamamura et al., 2007). With pretreatment (e.g. coagulation), NOM could be the major foulant if sedimentation is used after coagulation, while particle fouling through pore blockage and/or cake formation can be dominant when direct or inline filtration is used (Park et al. 2007, Desalination; Lee et al. 2006 Water science and Technology; Pikkarainen et al. 2004) .

In fact, studies have shown that small, neutral, hydrophilic fraction of NOM, which is the most difficult to be removed by coagulation and sedimentation (Sharp et al., 2006a, Sharp et al., 2004), contributed the most to microfiltration membrane fouling (Carroll et al., 2000, Fan et al., 2001). Some other studies demonstrated that NOM within 300-2000 and 20,000-40,000 Da were mainly responsible for the microfiltration

membrane fouling (Kim et al., 2006). Without sedimentation, the large amount of floc is expected to cause cake formation, increasing filtration resistance. The hydraulic resistance of the cake layer is a strong function of particle size and structure, which has been studied extensively by a group of Korean researchers (Lee et al., 2005b, Park et al., 2006a) (Choi et al. SPT, 2008, Lee et al. EST, 2000; Kim et al., JMS 2006, Cho et al. WST, 2005, Cho et al. Desalination, 2005, Lee et al. SPT, 2003). These researchers used either synthetic water with model foulants like hematite, polystyrene latex, and humic acid or real surface water during their investigations. By adjusting either coagulant dosage or mixing speed, they were able to obtain flocs of different size and fractal dimension for their filtrations. The general conclusion from these studies is that specific cake layer resistance increases with decreasing floc size and increasing floc fractal dimension assuming the floc structure. However, no research has included polymer flocculants, which could probably bring significant impacts on the coagulation/microfiltration system through affecting floc size, fractal dimension, and stickiness. Finally, as macromolecules, polymer flocculants may foul the membrane themselves when carried over to the membrane, which has been demonstrated in our previous work by filtrating synthetic water containing only polymer flocculants and necessary salts (Wang et al., 2011)

In the second part of our study reported here, we investigated the impact of polymer flocculants on MF membrane fouling after coagulation/flocculation pretreatment. Microfiltration of two surface waters was performed using both flat sheet and hollow fiber membranes under three different operation modes with and without the addition of polymer flocculants in the coagulation pretreatment.

## 6.2. Materials and Methods

### 6.2.1. Surface waters, membranes, and coagulant/flocculants

Two surface waters collected from the Grand Lake in Vinita, OK, and the Mississippi River in Minneapolis, MN, were used for this study. The Mississippi River water has high DOC and medium turbidity and the Grand Lake water has low DOC and low turbidity. Details for sampling, transportation, storage, and water quality of the two waters were presented in part I of the study. Filtration experiments were finished within 3 months and 6 months after water sample collection for the Grand Lake water and the Mississippi River water respectively. Water quality was routinely monitored and data showed no detectable change of the Grand Lake water, but the dissolved organic carbon (DOC) of the Mississippi River water decreased from  $10.8 \pm 0.8$  mg/L to  $8.0 \pm 0.2$  mg/L after 4 months of storage, possibly due to aggregation of colloidal DOC which would not be broke up by an intensive shaking before usage, consequently more DOC was removed by the syringe filtration using  $0.45 \mu\text{m}$  membrane before DOC measurement. The corresponding DOM (DOC and  $\text{UV}_{254}$ ) removals in this investigation were calculated based on the monitored DOC and  $\text{UV}_{254}$  data.

A flat sheet and a hollow fiber MF membrane (Pall Corporation, East Hills, NY) were tested. Properties of the two membranes are listed in Table 6-1. The flat sheet membrane is made of modified polyvinylidene fluoride (PVDF) with a nominal pore size of  $0.2 \mu\text{m}$ . The flat sheet membrane was cut into coupons of 2.5 cm diameter and stored at  $4^\circ\text{C}$  in ultrapure water ( $>18.0 \text{ M}\Omega$ ) generated by a Barnstead Epure purification

system (Barnstead Thermolyne, IA, USA) with water changed weekly. The hollow fiber membrane is made of PVDF as well, and the module has a length of 11 cm and a diameter of 2.5 cm. Fifteen fibers were potted inside the module with an effective fiber length of 9 cm. The fiber inside and outside diameters are 0.7 and 1.3  $\mu\text{m}$  respectively. The nominal pore size of the hollow fiber membrane is 0.1  $\mu\text{m}$ . The permeability of the hollow fiber membrane module was tested to be 182 LMH/PSI. The hollow fiber membrane module was not stored at 4 °C because of its frequent usage during research.

Table 6-1 Properties of the hollow fiber and flat sheet membranes

Parameter	Hollow fiber membrane	Flat Sheet Membrane
Membrane material*	PVDF	PVDF
Pore size*	0.1 $\mu\text{m}$	0.2 $\mu\text{m}$
Fiber I.D./O.D., mm*	0.7/1.3	NA
Number of fibers	15	NA
Outer surface area, ft <sup>2</sup> *	0.04	NA
Permeability, LMH/PSI**	182	346.5

\* Provided by Vendor

\*\* Measured

Polyaluminum chloride (PACl) (Southern Water Consultants, Decatur, AL) was used as the primary coagulant in all experiments. It contains 15.8% (w/w)  $\text{Al}_2\text{O}_3$  and is of 71.5% basicity. The polymer flocculants used include analytical grade poly (diallyldimethylammonium) chloride (pDADMAC) of 100-200 kDa and 400-500 kDa, poly (acrylic acid-co-acrylamide) (PACA) of 200 kDa and 520 kDa, and polyacrylamide (PAM) of 5000 kDa from Sigma Aldrich (St. Louis, MO). The electrophoretic mobility

and hydrodynamic diameter of the polymer flocculants can be found in our previous publication (Wang et al., 2011) .

### **6.2.2. Membrane filtration experiments**

Both hollow fiber and flat sheet membrane filtrations were adopted in this study to cover the practical applications in industry. Hollow fiber membrane filtration experiments were performed in a bench-scale coagulation-microfiltration system shown in Figure 6-1. The raw water was pre-settled for 2 hours to remove big particulate matter and the supernatant was taken as the feed water. A Filtertec peristaltic pump (SciLog, Middleton, WI) drew the feed water from a 4 liter feed reservoir to a 50 mL rapid mixing reactor, where the PACl and polymer flocculants were added by two syringe pumps. The rapid mixing was achieved using a magnetic stirring plate, a rapid mixing rate of 200 rpm was used for all the experiments. A second peristaltic pump transported the water from the rapid mixing reactor to a slow mixing reactor, from which the flocculated water was fed to the hollow fiber membrane module by a third peristaltic pump. The slow mixing was realized using a jar tester (Phillips & Bird) with a rate of 30 rpm. Two pressure sensors were located at the inlet and outlet of the hollow fiber MF module to measure pressures of the feed and permeate streams. The permeate water was collected in a container on a bench-top electronic balance, where the accumulated permeate mass was monitored to determine membrane flux. Signals from the two pressure sensors and the electronic balance were sent to the third pump, which was interfaced with a lab PC to collect data of the permeate flux and the transmembrane pressure (TMP) as well as control flow rate. The membrane unit was operated in dead-end mode.

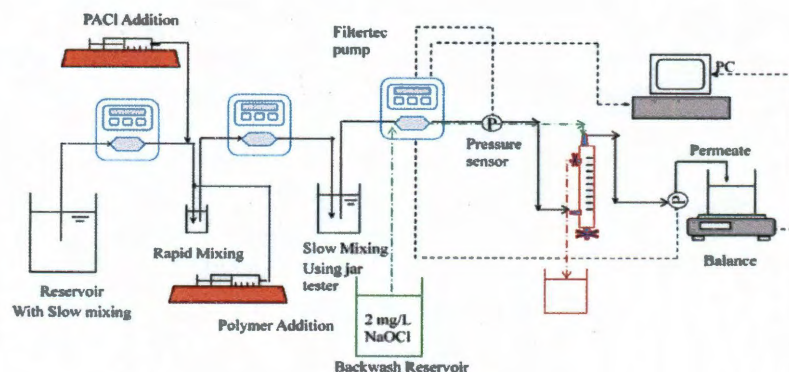


Figure 6-1 Schematic of hollow fiber membrane filtration

Hollow fiber membrane filtration experiments were performed both with and without sedimentation (i.e., direct filtration). In the direct filtration, the water went through the rapid mixing tank, the slow mixing tank, and the membrane module in sequence, hydraulic residence times of 1 and 20 min for the rapid and slow mixing reactors were used, respectively. Filtrations were run for five 30-min cycles with a flux of  $6.73 \times 10^{-5}$  m/s (242.2 LMH), which gave the system an approximate starting TMP of 2 psi and a room for TMP increase. Samples were collected from the permeate stream every 10 min for DOC and  $UV_{254}$  analysis. The membrane was backwashed after each cycle with 2mg/L NaOCl and chemically washed at the end of filtration. Three min's filtration of ultrapure water was performed between backwash and the next cycle, the average NTMP during this period was considered as the HIF. The chemical cleaning operated at 4 ml/min used two solutions: a mixture of 2000 mg/L NaOH and 2% NaClO and a 2% citric acid solution. At least 10 min's ultrapure water filtration was performed after the chemical cleaning to ensure a thorough foulant removal and an ordered membrane module. In filtrations with sedimentation, the water was coagulated using a Jar Tester separately. The supernatant was collected for filtration after 1 hr's sedimentation

using the setup after the third pump in Figure 6-1. The  $6.73 \times 10^{-5}$  m/s flux was used to keep it consistent with direction filtration, and the total filtration time was 150 min. Because of the low membrane fouling rate, no backwash was used for filtrations with sedimentation.

The flat sheet membrane filtration was done with the Grand lake water and earlier than the hollow fiber membrane filtration with the Mississippi river water. The flat sheet membrane filtration procedure was the same as the hollow fiber membrane filtration procedure except that an Amicon stirred cell (Millipore, Billerica, MA) with a 10 ml total volume was used as the microfiltration unit. Both inline and direct filtrations were tested. However, no significant difference was seen between with and without polymer flocculant conditions for the inline mode, which was also the reason that inline mode was not tested with hollow fiber membrane filtration. The inline filtration means that the water goes directly from the rapid mixing to the microfiltration. Filtrations were run for 50 min with a flux of  $2.38 \times 10^{-4}$  m/s (856.1 LMH). Samples were collected and analyzed in the same way as for the hollow fiber membrane filtration. A piece of new membrane was used for each filtration. All experiments were run at ambient temperature of 22 °C. Because of the limited amount of water sample, only experiments with absurd results were repeated.

According to the jar tests in our previous study, the cost effective dosages were 15mg/L PACl and 1mg/L polymer for the Mississippi River water and 10mg/L PACl and 1mg/L polymer for the Grand Lake water. DOC concentration and UV absorbance at 254 nm of samples from all experiments were measured using a total organic carbon analyzer (TOC-V<sub>CSH</sub>, Shimadzu Scientific Instruments, Kyoto, Japan) and an UV-Vis



spectrophotometer (Ultrospec 2100 Pro, Shimadzu Scientific Instruments, Kyoto, Japan) respectively. Turbidity was measured using a 2100N Turbidimeter (Hach, Loveland, Colorado).

## **6.3. Results and discussion**

The effect of different polymer flocculants on membrane fouling was evaluated with both Vinita and Mississippi River water.

### **6.3.1. Hollow fiber membrane filtration with Mississippi River water**

#### **6.3.1.1. Filtration after 1 hr's sedimentation**

Five polymers were used in the hollow fiber membrane filtration of the Mississippi River water with sedimentation including 5000-6000 kDa PAM, 100-200 and 400-500 kDa pDADMACs, and 200 and 520 kDa PACAs. Figure 6-2 compares the normalized transmembrane pressure (NTMP), permeate DOC concentration and  $UV_{254}$  measured during different experiments. Without any pretreatment, the membrane fouled very quickly with the NTMP reaching 3.45 after only 30 min of filtration. Coagulation using 15 mg/L PACl greatly reduced fouling, but the TMP still rose by 53% after 150 min of filtration. Among the five polymers tested, the two pDADMACs showed significant reduction in fouling rate, with only 13 and 29 % increase in TMP after 150 min filtration for the 400-500 kDa and the 100-200 kDa pDADMAC, respectively. The PACAs and PAM, however, increased fouling notably compared to when PACl alone was used. Due to the similarity of the permeate DOC and  $UV_{254}$  level of samples during

the 150 min filtration, average values of samples from one filtration are presented in Figure 6-2.

The average DOC and UV<sub>254</sub> removals are 49.9, 56.3, 56.5, 51.3, 50.3, 54.7% and 67.6, 66.6, 69.1, 69.8, 64.4, 65.3% for PACl only, 5000-6000 kDa PAM, 400-500 kDa pDADMAC, 100-200 kDa pDADMAC, 200 kDa PACA, and 520 kDa PACA respectively. The three relatively larger polymers (i.e. 5000-6000 kDa PAM, 400-500 kDa pDADMAC, and 520 kDa PACA) enhanced DOC removal compared to PACl only condition, whereas the two relatively smaller polymers (i.e. 100-200 kDa pDADMAC and 200 kDa pDADMAC) did not change the DOC removal. Comparisons between results from filtration with sedimentation (Figure 6-2) and those from coagulation tests in Chapter 5 (Figures 5-2 to 5-4) indicated a consistency in DOC and UV<sub>254</sub> removals for Mississippi river water. The difference might be ascribed to better flocculation ability of the larger polymers which subsequently lead to more NOM incorporation and floc sedimentation. However, only the two pDADMACs improved the UV<sub>254</sub> removal because of their negative charge neutralization ability while PAM did not affect UV<sub>254</sub> removal. The negatively charged PACAs even worsened UV<sub>254</sub> removal, which is probably caused by their competition with negatively charged humic substances when neutralized by the positively charged Al species.

Apparently, the membrane fouling was correlated with UV<sub>254</sub> removal. The two pDADMACs, which slightly increased UV<sub>254</sub> removal, also reduced membrane fouling. Contrarily, the two PACAs and the PAM, which did not help UV<sub>254</sub> removal, increased the membrane fouling. Therefore, it is assumed that the humic substance which is usually characterized using UV<sub>254</sub> was the major membrane foulant when coagulation and

sedimentation were applied before microfiltration. Although no data about DOC and UV<sub>254</sub> removal before 0.2 µm membrane filtration were available, it is inferred that the cationic pDADMACs removed more UV<sub>254</sub> even before the 0.2 µm membrane filtration.

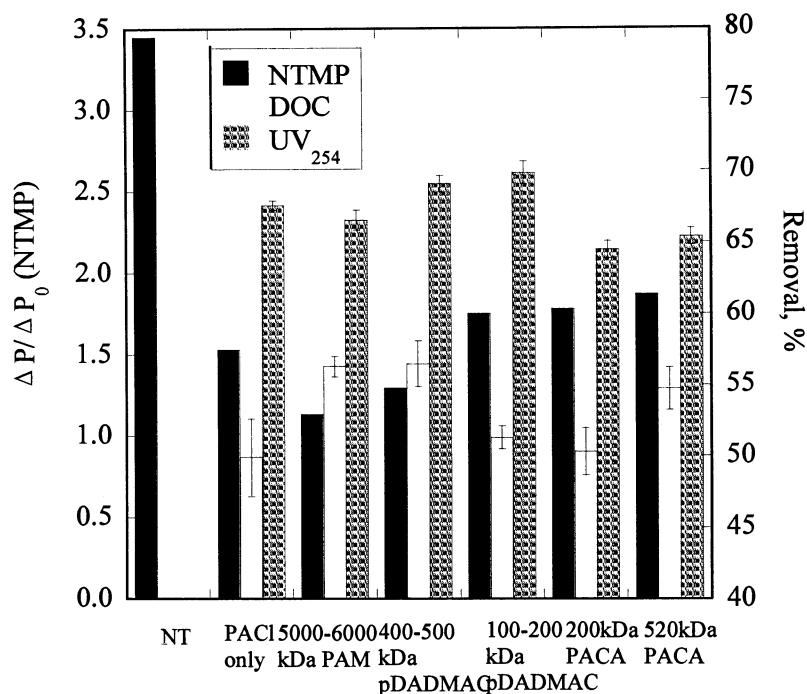


Figure 6-2 Filtration after 1 hr's sedimentation using 15mg/L and 1mg/L polymer.

The filtration time for NT condition is 30 min and 150 min for all other conditions. The DOC and UV<sub>254</sub> removal rate for NT condition were 17.4 % and 0.6 % respectively.

The effect of coagulant/polymer concentration on membrane fouling was also investigated with Mississippi River water using hollow fiber membrane. Three polymer flocculants including 400-500 kDa pDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM were tested. Several PACl dose (mg/L)/polymer dose (mg/L) groups were used for coagulation: 0/15, 0.5/15, 1/20, 1/10, 2/15. Figure 6-3 (a) and (b) present the results of

NTMPs and removals of DOC and  $UV_{254}$  for filtrations after 1 hr's sedimentation using different coagulant and polymer concentrations. In general, the 400-500 kDa pDADMAC reduced membrane fouling under all conditions compared to using PACl only, both the 520 kDa PACA and the 5000- 6000 kDa PAM increased membrane fouling regardless of the coagulant and polymer doses applied. Increased PAM/PACl ratio resulted in increased membrane fouling. However, variation of polymer/PACl ratios did not affected membrane fouling much for the 400-500 kDa pDADMAC and the 520 kDa PACA.

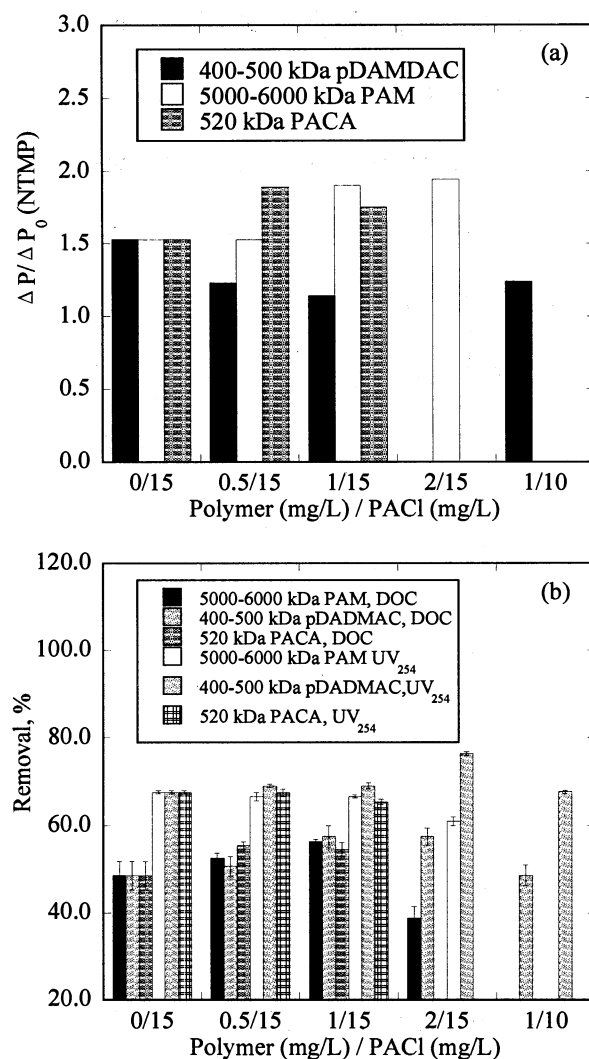


Figure 6-3 Effect of coagulant/polymer concentration on membrane fouling for filtration after 1 hr's sedimentation

A general trend can be observed in Figure 6-3 (b) is that the DOC removal was increased with increasing polymer flocculants dosage (from 0.5 to 2 mg/L) when PACl concentration was kept at 15 mg/L except when 2 mg/L PAM and 15 mg/L PACl were used. Besides, a reduction in DOC removal was observed when 1 mg/L 400-500 kDa pDADMAC and 10 mg/L PACl were used. When 15 mg/L PACl was used, neither the

neutral PAM nor the anionic PACA increased  $UV_{254}$  removal, the  $UV_{254}$  removal was even reduced when 2 mg/L PAM was used. But the  $UV_{254}$  removal was enhanced for all the condition except when 1 mg/L 400-500 kDa pDADMAC and 10 mg/L PACl were used. The DOC and  $UV_{254}$  removals shown in Figure 6-3 are consistent with the results from coagulation experiments in Chapter 5 (see Figures 5-2 to 5-4).

The enhanced DOC removal by polymers under most conditions can be attributed to the improved coagulation/flocculation and subsequent better sedimentation as observed in the jar tests; the reduced DOC removals at polymer/PACl ratio of 2/15 for PAM and 1/10 for pDADMAC are attributed to the overdosed PAM and insufficient PACl dosage respectively. On the other hand, the removal of  $UV_{254}$  removal is primarily determined by charge neutralization as discussed in Chapter 5. Therefore, the 400-500 kDa pDADMAC generally helped remove  $UV_{254}$  because of its positive charge. The reduction of  $UV_{254}$  removal at polymer/PACl ratio of 1/10 is again attributed to the insufficient PACl dosage. The neutral PAM and the negatively charged PACA generally did not affect the  $UV_{254}$  removal.

#### **6.3.1.2. Direct filtration**

Results of direct filtrations with 15mg/L PACl and 1mg/L polymers are shown in Figure 6-4. All polymers tested greatly increased membrane fouling compared to when PACl was used alone. The membrane fouling rate follows the order of 5000-6000 kDa PAM > 400-500 kDa pDADMAC > 100-200 kDa pDADMAC > 520 kDa PACA > 200 kDa PACA > PACl only. The membrane fouling seems to depend on the polymer charge and molecular weight. The negatively charged polymers caused less fouling than the non-ionic and positively charged polymers. For the same polymer type, the higher MW one

caused more fouling. The PAM fouled more than the positively charged pDADMACs, probably because of its much higher MW. Compared to the big differences in NTMPs between different conditions, the differences in DOC and UV<sub>254</sub> removals between different conditions were much smaller, which were 55.9, 54.1, 54.0, 54.3, 59, 57.5% and 66, 65.2, 68, 65, 67.3, 66.8% for PACl only, 5000-6000 kDa PAM, 400-500 kDa pDADMAC, 100-200 kDa pDADMAC, 200 kDa PACA, and 520 kDa PACA respectively. Statistical differences from others at 95% confidence level was found for DOC removal by only 200 kDa PACA and UV<sub>254</sub> removal by 400 kDa pDADMAC and 200 kDa PACA. The better DOC and UV<sub>254</sub> removal by 200 kDa PACA was probably due to its stronger hydrogen bonding formation ability caused by the 80% content of acrylic acid, which was also discussed in our previous publication (Wang et al., 2011). The 400-500 kDa pDADMAC only improved the UV<sub>254</sub> removal significantly, which should be attributed to its positive charge and consequent charge neutralization with the negatively charged humic substance.

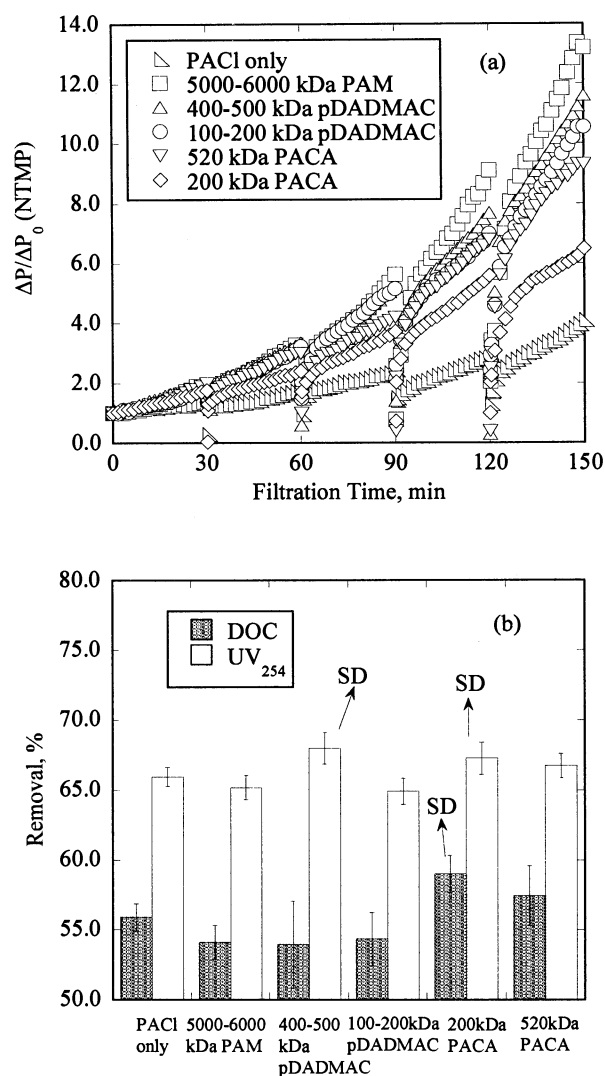


Figure 6-4 Direct Filtration using 15mg/L PACl and 1mg/L polymer, SD represents statistically different from others at 95% confidence level.

The effect of coagulant/polymer concentration on membrane fouling in direct mode filtration was again investigated using five polymer/PACl ratios (0/15, 0.5/15, 1/20, 1/15, 1/10, and 2/15) for 400-500 kDa pDADMAC, 5000-6000 kDa PAM, and 520 kDa PACA. The results are presented in Figure 6-5, where a trend of membrane fouling



shared by all the polymers was observed. Membrane fouling followed the order of  $1/20 \geq 1/10 > 2/15 \approx 0.5/15 > 0/15$  in terms of polymer/PACl ratio. Notice that membrane fouling at 15 mg/L PACl and 1 mg/L polymers (Figure 6-4) was much higher than other concentration conditions (Figure 6-5). The filtration experiments with 15 mg/L PACl and 1 mg/L polymers were carried out several months ahead of the experiments with various concentrations of PACl and polymers. As explained previously, the dissolved organic carbon (DOC) of the Mississippi River water experienced a reduction after several months of storage, possibly due to aggregation of colloidal DOC which would not be broke up by an intensive shaking before usage, consequently more DOC was removed by the pre-sedimentation before filtration experiments. This difference in DOC levels after pre-sedimentation was probably the reason that membrane fouling at 15 mg/L PACl and 1 mg/L polymers (Figure 6-4) was much higher than other concentration conditions. The corresponding DOC and  $UV_{254}$  removals were adjusted based on monitored DOC data and are presented in Figure 6-6. Neither DOC nor  $UV_{254}$  removal was changed obviously when 15 mg/L PACl was used. But both the DOC and  $UV_{254}$  removals were changed significantly when the PACl dosage was altered. The DOC and  $UV_{254}$  removals were increased at polymer/PACl ratios of  $1/20$  and but decreased at  $1/10$ . A general order of  $1/20 > 0/15 \approx 0.5/15 \approx 2/15 > 1/10$  was found for both DOC and  $UV_{254}$  removal in terms of polymer/PACl ratios.

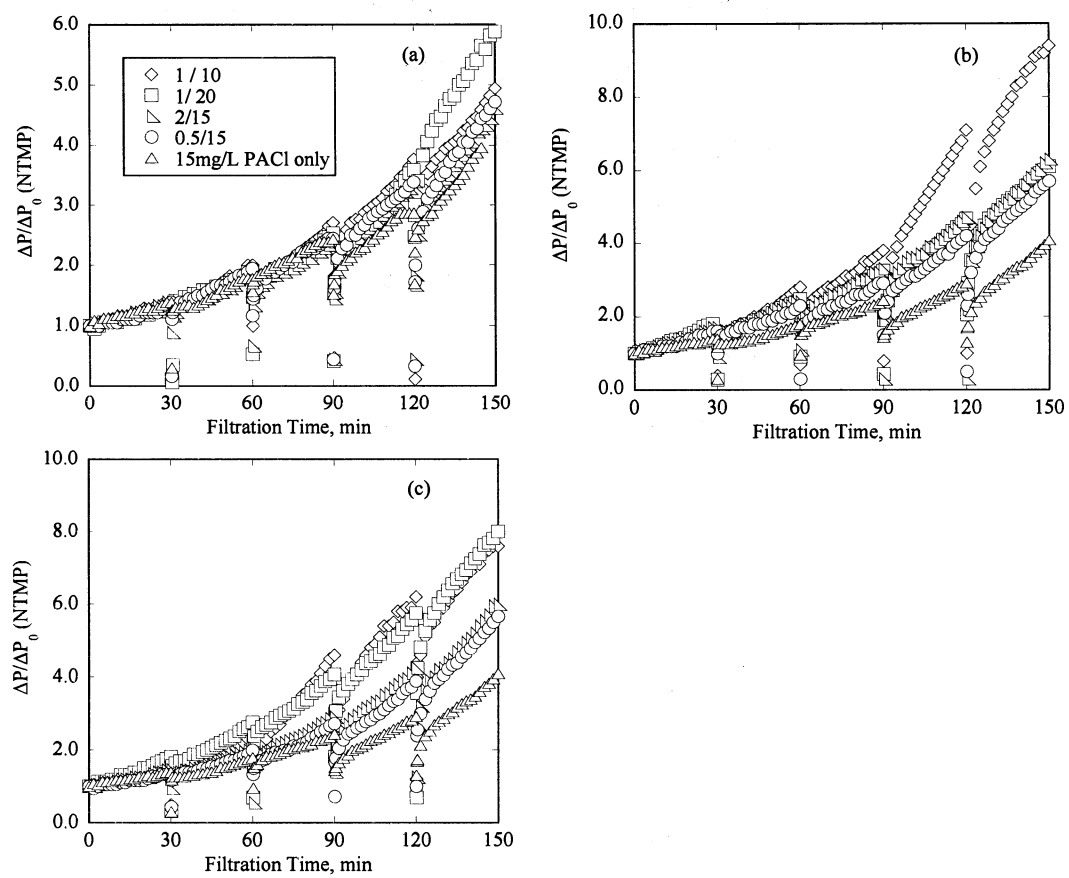


Figure 6-5 Effect of coagulant/flocculant concentration on direct mode membrane fouling.

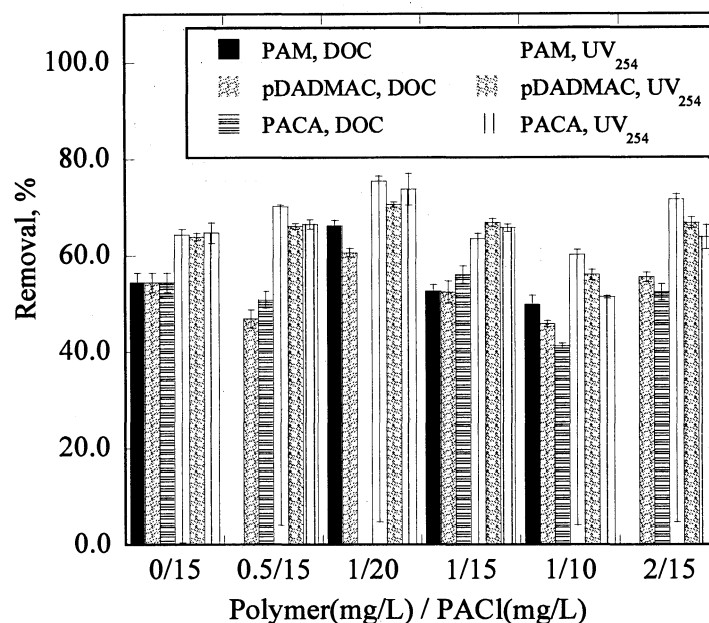


Figure 6-6 Effect of coagulant/flocculant concentration on membrane fouling in direct filtration of Mississippi river water.

The high membrane fouling rate by using a ratio of 1/20 can be ascribed to the high rate of solid production, whereas the high membrane fouling rate by using a ratio of 1/10 might be due to the inefficient incorporation of polymers into flocs, consequently more polymer attached on the membrane surface and caused more irreversible fouling. Notice that the NTMPs at polymer/PACl ratio of 1/15 in Figure 6-4 are much higher than those in Figure 6-5 at various polymer/PACl ratios; this is because experiments in Figure 6-4 were performed 3 months earlier than those in Figure 6-5. The quality of source water has changed during the research period by forming more colloidal DOC which was removed in the pre-sedimentation. As demonstrated above, the mechanism for negatively charged UV<sub>254</sub> removal is mainly charge neutralization. The higher PACl dosage was applied, the more positively charged Al species existed in the solution, and the more

UV<sub>254</sub> was removed, which is proved in Figure 6-6 at polymer/PACl ratio of 1/20. With the lowest Al species content, UV<sub>254</sub> was removed the least at polymer/PACl ratio of 1/10. The enhanced DOC removal rate was also attributed to better coagulation/flocculation at polymer/PACl ratio of 1/20. The slight variance of DOC removal using 15mg/L PACl and polymers was probably due to the difference in rejection by the cake layer or membrane.

#### **6.3.1.3. Hydraulically Irreversible Fouling**

The hydraulically irreversible fouling (HIF) was determined for direct filtrations using hollow fiber membrane. The HIF during filtration of 15mg/L PACl coagulated water was marked in Figure 6-7. The NTMP first raised rapidly to the HIF level, then increased slowly during the rest of filtration.

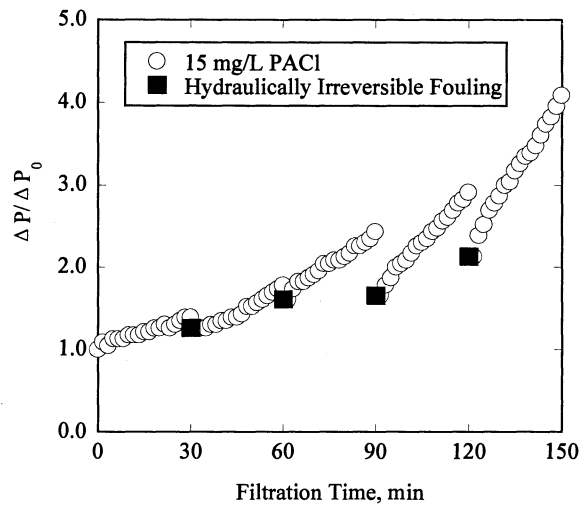


Figure 6-7 Hydraulically irreversible fouling during direct hollow fiber membrane filtration

The HIFs of all conditions and net NTMP increase during each cycle of filtration were plotted in Figure 6-8 (a) and (b) respectively. Obviously, the HIF and net NTMP increase followed similar trend to membrane fouling shown in Figure 6-4 and 5-5. However, the increase rates were different with faster increase of HIF and slower increase of net NTMP increase when polymers were used. This indicates that the polymers had slightly greater impact on HIF than on net NTMP increase. Polymers from either the solution (residual polymer) or the flocs can strengthen the stickiness between flocs and membrane surface causing more HIF.

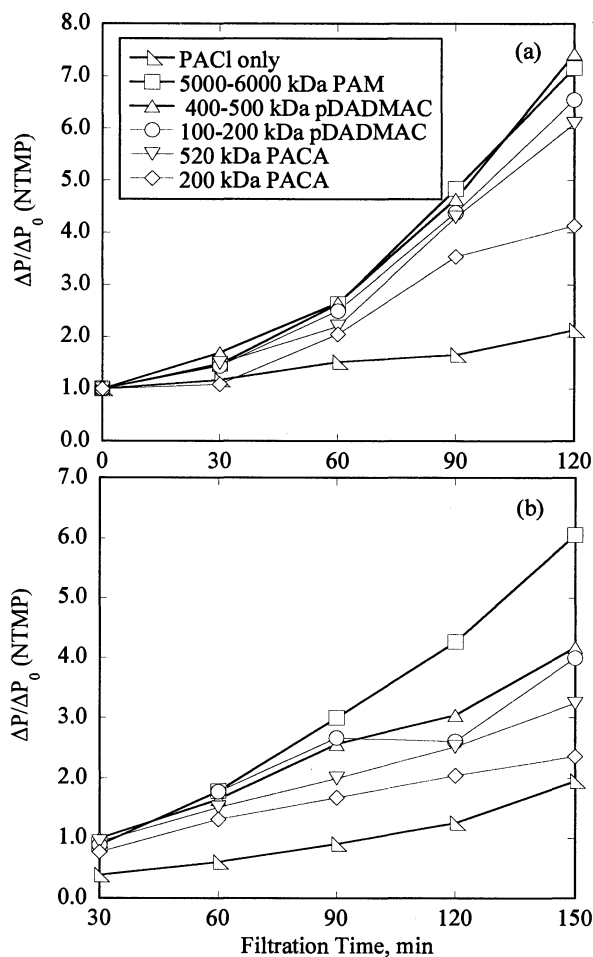


Figure 6-8 HIF (a) and net NTMP (b) increase during direct filtration with 15 mg/L PACl and 1 mg/L polymer

Correlating the floc size and fractal dimension results from the part of this study with the membrane filtration results, it is obvious that polymer flocculants led to larger floc size and smaller floc fractal dimension, which further incurred higher membrane fouling. This is contrary to the result of previous study (Lee et al., 2003b, Lee et al., 2005b, Park et al., 2006a). It is hypothesized that the flocs with more fractal structure when polymers are used could be compressed to a denser cake layer causing a higher

filtration resistance. The similar increase rate of NTMPs using different polymers during each filtration cycle shown in Figure 6-8 (b) can also be explained by the similar floc sizes and fractal dimensions.

### **6.3.2. Flat Sheet Membrane Filtration of Vinita Water**

Filtrations of the Grand Lake water were performed before experiments with the Mississippi water using flat sheet membrane under both direct and inline modes. The flat sheet membrane was used to cover real applications in industry. The results are presented in Figure 6-9. With direct filtration, both pDADMACs and PACAs were able to slightly reduce membrane fouling compared to using PACI only, and the difference between with and without polymers was of statistical significance at 95% confidence level. But the 5000-6000 kDa PAM increased the fouling rate considerably with an NTMP of 5.6 at the filtration end. The DOC and UV<sub>254</sub> removal rate were 30.5, 31.8, 41.8, 40.6, 43.0, 42.5% and 54.0, 54.5, 61.6, 61.8, 56.6, 57.2% for PACI only, 5000-6000 kDa PAM, 400-500 kDa pDADMAC, 100-200 kDa pDADMAC, 200 kDa PACA, and 520 kDa PACA respectively. The 5000-6000 kDa PAM affected neither the DOC nor the UV<sub>254</sub> removal. The PACAs lead to some DOC removal but negligible UV<sub>254</sub> removal, while the pDADMACs slightly enhanced both DOC and UV<sub>254</sub> removal compared to using PACI only. The results for PAM and pDADMACs are consistent with those from the jar tests in the first part of our study: no effect for 5000-6000 kDa PAM and around 10% additional DOC removal for the pDADMACs. The negatively charged PACAs, however, behaved differently from that observed in the jar tests. Some DOC removal improvement was observed in filtration experiment which was not found in jar tests, the improvement is

possibly due to small DOM removal by the cake layer formed on membrane surface. Considering that PAM had no impact on either DOC or UV<sub>254</sub> removal, the increased fouling shown in Figure 6-9 can be attributed to either the carryover of PAM molecules or change in floc properties (i.e. size and fractal dimension).

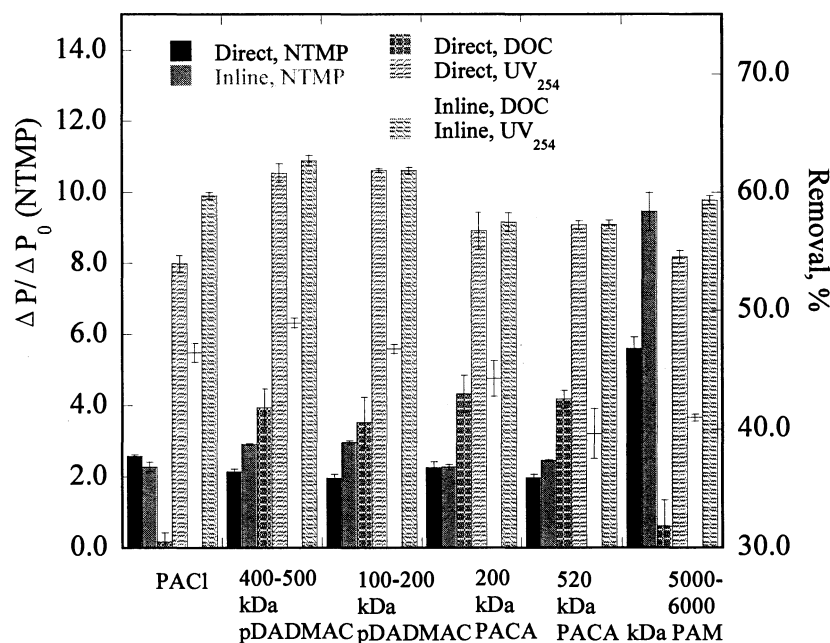


Figure 6-9 Normalized TMP, DOC, and UV<sub>254</sub> removal of Vinita water

With inline filtration, all the polymers lead to increased membrane fouling especially the 5000-6000 kDa PAM. Obviously, no polymer improved DOC removal and only pDADMACs slightly increased the UV<sub>254</sub> removal due to their positive charges. Due to the lack of slow mixing under inline mode, on one hand, the flocs should be much smaller than that under direct mode which can clog more membrane pores and increase membrane fouling; on the other hand, more exposure of polymers to the membrane surface is possible which can increase the membrane fouling. Moreover, there may not be



sufficient contact time for all polymer molecules to be incorporated into floc particles. The most severe fouling caused by PAM is possibly due to the even more exposure because of its larger molecule size. Some increase in DOC and  $UV_{254}$  removal was observed for using PACl only, PAM, and pDADMACs which might also be attributed to the smaller flocs. Consequently, these smaller flocs might clog more membrane pores and prevent more polymers from going through the membrane.

## 6.4. Conclusions

The effect of polymer flocculants on membrane fouling in the coagulation-microfiltration system was systematically evaluated under various conditions. Polymers were found to worsen membrane fouling under most conditions, even though they may bring slight benefit for NOM removal. Only the pDADMACs reduced membrane fouling for filtrations with sedimentation the main factor controlling membrane fouling is attributed to the residual colloidal NOM. In the direct mode hollow fiber filtration, hydraulically irreversible fouling was found to affect membrane fouling the most probably due to the accumulation of polymers on the membrane surface; membrane fouling is highly affected by polymer/PACl ratio. With higher PACl dosage, higher membrane fouling can be caused by more solid generated from higher PACl dosage. With lower PACl dosage, higher membrane fouling can be caused by higher hydraulically irreversible fouling due to higher exposure of membrane surface to polymer. The membrane fouling was found to be higher with increased floc size and reduced floc fractal dimension.

***Chapter 7 Impact of Polymer Flocculants on  
Floc Properties and Cake Layer Structure<sup>4</sup>***

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<sup>4</sup> Manuscript prepared for submission to Water Research

## 7.1. Introduction

Coagulation is now a widely accepted pretreatment for microfiltration (MF) in drinking water treatment due to its capability of removing both particulate matter and dissolved organic carbon (DOC), which are primary foulants of MF membranes. As a result, membrane performance including both treated water quality and membrane flux is enhanced. Polymer flocculants, which are commonly used in the conventional coagulation/flocculation/sedimentation process to improve flocculation and sedimentation, are sometimes used in the coagulation-MF process. The assumption is that polymers would improve performance of the coagulation-MF process through the same mechanisms as in the conventional treatment process.

Particle flocculation by polymers normally occurs through bridging, charge neutralization, and depletion flocculation, or a combination of these mechanisms (Bolton and Gregory, 2007). The bridging and charge neutralization are much more significant in the water treatment field than the depletion flocculation, because the later depends on the concentration of free polymer flocculant (Besra et al., 2002, Jang et al., 2004). Cationic polymers flocculate through both charge neutralization and bridging flocculation. With proper dosage, bridging, charge neutralization, and electrostatic patch flocculation occurs when charge density is low, medium, and high respectively (Zhou and Franks, 2006). The mechanism for nonionic and anionic polymers is primarily bridging flocculation (Nasser and James, 2006) through interactions such as hydrogen bonding (Griot and Kitchener, 1965, Rubio and Kitchener, 1976).

There are several issues concerning using polymers in the coagulation-microfiltration process: (1) being macromolecules of large molecular weight, polymers might foul the membrane directly when they are overdosed; (2) polymer flocculants might not improve NOM and turbidity removal because NOM is mainly removed by primary coagulant and microfiltration pores are small enough to offset the impact of polymer flocculants on turbidity removal. These issues have been address in our previous studies. The results indicated that free polymers might foul membrane significantly after 1 hr's filtration even at 0.05 mg/L regardless of polymer charge, and polymer flocculants have least impact on NOM removal but caused significantly more membrane fouling except when cationic polymers are used for filtrations after sedimentation. Our study showed that polymer flocculants significantly increased floc size and decreased floc fractal dimension. The increased membrane fouling could have been caused by two primary reasons: (1) the changed floc properties (size and fractal dimension) result in different compressibility of the flocs and a denser cake layer; (2) the polymer flocculants incorporated into the flocs might enhance the interaction between floc and membrane surface and the interaction between floc and floc in the cake layer.

A series of studies has focused on the relations of floc properties to cake layer properties such as cake layer density and specific cake resistance (Cho et al., 2005, Choi et al., 2008, Lee et al., 2000, Lee et al., 2005b, Park et al., 2006b, , 2007) through both experimental work and mathematical modeling. Very few studies tried to investigate the interaction between flocs and membrane surface. An example of such studies is the

research by Lin et al. (2011), during which smaller flocs were found to attach onto membrane surface more easily in a submerged anaerobic membrane bioreactor (Lin et al., 2011). However, very limited information can be obtained from these studies. Consequently, the study reported in this paper aims at: (1) evaluate the impact of polymers on floc attachment efficiency onto membrane surface; (2) identify the mechanism of polymers' impact on floc attachment efficiency; (3) establish the connection between polymers' impact on membrane fouling and impact on floc attachment efficiency on membrane surface.

## **7.2. Materials and Methods**

### **7.2.1. Membrane and Surface Water**

A flat sheet membrane (Pall Corporation, East Hills, NY) made of modified polyvinylidene fluoride (PVDF) with a nominal pore size of 0.2  $\mu\text{m}$  was used in this study. Characterizations of the PVDF membrane can be found in a previous publication (Wang et al., 2011). The membrane was cut into rectangles of 2 inch in width and 4 inch in length. The membrane samples were wetted with 50% iso-propanol solution and then rinsed with ultrapure water generated by a Barnstead Epure purification system (Barnstead Thermo Scientific, IA, USA) until no iso-propanol was smelled. Afterward, the clean membrane samples were stored at 4 °C in ultrapure water before usage. The membranes were prepared every 3 days to prevent possible contamination. The raw water used in this study was Lake Houston water taken from the intake of Houston Water Purification Plant in July of 2010, and some key water quality data are presented in Table

7-1. As can be seen, the Lake Houston water has medium concentrations of both DOC and turbidity.

Table 7-1 Key parameters of Lake Houston water

Parameters	Value
DOC, mg/L	5.95±0.3
Alkalinity, mg/L as CaCO <sub>3</sub>	68±0.2
pH	8.17
Turbidity, (NTU)	4.44±0.11
UV <sub>254</sub> absorbance, cm <sup>-1</sup>	0.186±0.002

### 7.2.2. Primary Coagulant and Flocculants

Polyaluminum chloride (PACl) obtained from Southern Water Consultants (Decatur, AL) was used as the primary coagulant. The PACl contains 15.8% (w/w) Al<sub>2</sub>O<sub>3</sub> with a 71.5% basicity. Three types of analytical grade polymer flocculants of different charges were purchased from Sigma Aldrich (St. Louis, MO): poly (diallyldimethylammonium) chloride (pDADMAC) of 100 - 200 and 400 - 500 kDa, poly (acrylic acid-co-acrylamide) (PACA) of 200 and 520 kDa, and polyacrylamide (PAM) of 5000-6000 kDa. The 200 kDa PACA and the 520 kDa PACA contain 80% and 20% acrylic acid respectively. Electrophoretic mobility and hydrodynamic radius of each polymer were determined by phase analysis light scattering (PALS) and dynamic light scattering (DLS) using a Zen3600 Zetasizer Nano (Malvern Ltd., Malvern, UK). Details

of the characterization methods and results can be found in a previous publication (Wang et al., 2011).

### 7.2.3. Coagulation/Flocculation

The coagulation/flocculation experiments were performed at 22 °C in a standard jar test apparatus (Phillips & Bird) for dosage optimization based on organic matter removal. Rapid mixing at 100 rpm was set for 2 min followed by slow mixing at 30 rpm for 20 min, after which mixing was stopped for sedimentation. PACl was dosed at the onset of the rapid mixing, and the polymer flocculants were added 30 seconds afterwards. PACl dosages ranging from 0 to 25 mg/L as  $\text{Al}_2\text{O}_3$  were applied with 0, 0.5, and 1 mg/L of each polymer flocculant. Samples were collected from the supernatant after 60 min's sedimentation and filtered through 0.2  $\mu\text{m}$ -pore-diameter PVDF membranes housed in syringe filters. The first 5 ml filtrate of each sample was discarded to saturate the NOM adsorption capacity of the membrane. The filtered samples were then analyzed for dissolved organic carbon (DOC) concentration and  $\text{UV}_{254}$  absorbance.

DOC concentration and  $\text{UV}_{254}$  absorbance were measured using a total organic carbon analyzer (TOC-V<sub>CSH</sub>, Shimadzu Scientific Instruments, Kyoto, Japan) and an UV-Vis spectrophotometer (Ultrospec 2100 Pro, Shimadzu Scientific Instruments, Kyoto, Japan) respectively.

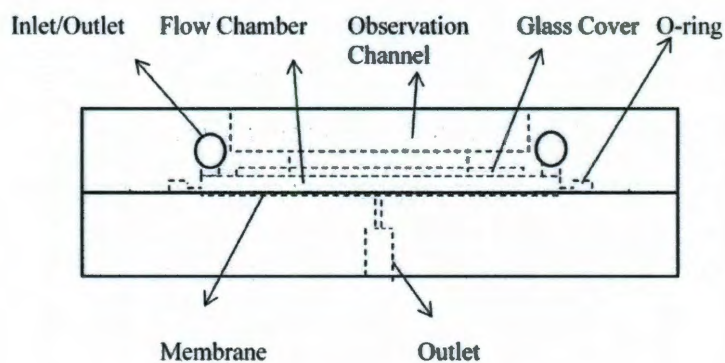
## **7.2.4. Membrane Reactor Design**

To investigate the mechanism of membrane fouling when polymer flocculants are used, two membrane reactors were designed: a cross flow module and a detachable hollow fiber membrane module.

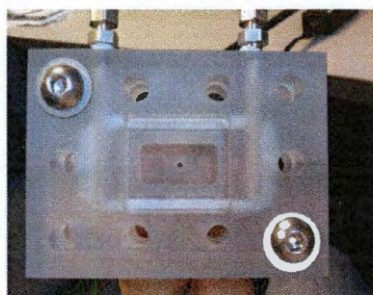
### **7.2.4.1. Flow Module Design**

A special device, which provides a flow chamber, a glass cover, and an observation channel as shown in Figure 7-1 (a), was designed to investigate the floc attachment onto membrane surface. During operation, a piece of membrane is placed between the two parts, an o-ring is utilized to seal the system, and the chamber is fastened with bolts and nuts. The water flows into either of the inlets and out from another on the upper part of the chamber. The permeate is collected from the outlet on the lower part of the chamber. After filtration, either the chamber or the membrane can be taken to microscopic observation. An image of the upper part of the flow chamber is presented in Figure 7-1(b) for a better view.





(a) Schematic of the flow chamber



(b) Image of the upper part of the flow chamber

Figure 7-1 Schematic and image of the cross flow module

#### 7.2.4.2. Detachable Hollow Fiber Membrane Module

One way to determine whether polymer flocculants are a cause of membrane fouling is to find out whether the polymers are accumulated on the membrane surface. This requires monitoring the fouling layer using a membrane autopsy technique that can specifically identify polymer flocculants in the fouling layer. Accordingly, a special hollow fiber membrane filtration module was designed to allow time resolved sampling of the fibers. A picture of the new module (referred to as detachable module hereafter) is shown in Figure 7-2 (b). The new module was designed to have exactly the same functions as the conventional module.



(a), Conventional module



(b), New module

Figure 7-2 Comparison of conventional and new hollow fiber membrane filtration modules

### 7.2.5. Floc Attachment Efficiency Evaluation Protocol

Before experiments, the raw water was pre-settled to a fixed turbidity of 1.9 NTU. Coagulation and flocculation was conducted with 2 min of rapid mixing and 20 min of slow mixing, at the end of which, the coagulated water was pumped through the cross-flow chamber. The experimental schematic for measuring floc attachment efficiency is presented in Figure 7-3. Attachment efficiencies of floc particles formed with and without polymer flocculants on membranes with and without adsorbed polymers were evaluated.

#### 7.2.5.1. Effect of polymer adsorption on membrane on floc particle attachment

To investigate how polymer contamination of the membrane surface affect floc particle attachment, floc particle deposition/attachment on membrane samples pre-exposed to polymer flocculants was compared to that on clean membrane samples. To preload the membrane with polymer flocculants, a polymer flocculant solution of 0.5 mg/L was filtered through the membrane at a flow rate of 20 ml/min in a dead-end mode for 60 min, i.e., circulation pump was turned off. The final loading of polymers was  $0.031\text{mg/cm}^2$ . After polymer loading, the module was emptied and the circulation of flocculated water through the flow chamber started at the end of 20 min's slow mixing at a cross-flow rate of 20 ml/min. Particle deposition on the membrane surface was recorded by the CCD camera *in situ*. Videos were taken every 5 minutes. The slow mixing was kept constant at 30 rpm until the end of 120 min's circulation. A HPLC pump drew the permeate at a constant flow rate of 0.85 ml/min with a corresponding flux of  $7.31 \times 10^{-6}$  m/s. to provide a constant permeate drag force; the permeate was recirculated back to the flocculation tank. After the 120 min circulation, the floc particles accumulated on the membrane surface were collected, and the particle suspension was filtered through a pre-weighed  $0.45\text{ }\mu\text{m}$  filter. The filter was dried overnight at ambient condition and weighed again. The mass of floc particles attached on the membrane was calculated from the weight difference between the clean filter and the particle laden filter. A piece of new membrane was used for each experiment. For quality control of weight measurement, a piece of  $0.45\text{ }\mu\text{m}$  membrane was monitored for each experiment throughout the research. The monitoring result showed a maximum variation 0.37. The calculation method is presented below

$$\text{Variation} = \frac{\text{Maximum(Minimum) weight} - \text{Average Weight}}{\text{Average Weight}} \times 100$$

#### 7.2.5.2. Attachment of polymer-containing floc particles on clean membrane

Floc particles formed in the presence of a polymer flocculant will have the polymer in them. The attachment efficiency of floc particles formed in the presence of a polymer flocculant on clean membrane surface was compared to that of floc particles formed in the absence of polymer flocculants. Again, the circulation started at the end of 20 min's slow mixing with a peristaltic pump at a flow rate of 20 ml/min. The slow mixing was kept constant at 30 rpm until the end of experiments. A HPLC pump drew the permeate at a flow rate of 0.85 ml/min to provide a constant drag force, the permeate was sent back to the flocculation tank. For each experimental condition, six filtration runs were performed with filtration time of 30, 60, 90, 120, 150, and 180 min to quantitatively measure floc deposition as a function of time. A piece of new membrane was used for each filtration experiment. During the filtration, videos were recorded every 5 min. After the filtration run, the flocs accumulated on the membrane surface were collected and particle suspensions filtered through a pre-weighed 0.45  $\mu\text{m}$  filter, and then the filter was dried overnight at ambient condition before another weighing. The net weight of flocs attached inside the chamber was then acquired as the weight difference.



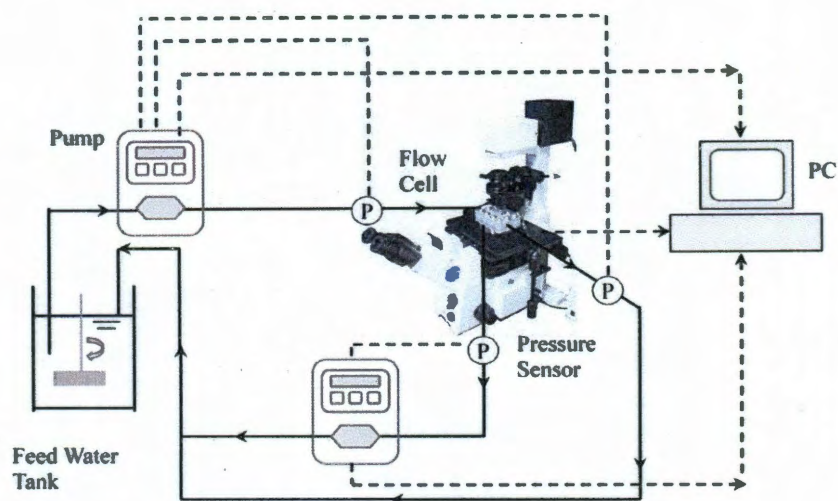


Figure 7-3 Experimental schematic of floc stickiness evaluation

#### 7.2.6. Filtration Protocol with the Detachable Module

Filtration experiments with the detachable hollow fiber membrane module were performed in direct filtration mode. A schematic of the experimental setup is presented in Figure 7-4. Basically, the feed water goes through the rapid mixing tank, the slow mixing tank, and the membrane module in sequence, hydraulic residence times of 1 and 20 min for the rapid and slow mixing reactors were used, respectively. Filtration experiments were run for five 30-min cycles with a flux of  $6.73 \times 10^{-5}$  m/s (242.2 LMH). The membrane was backwashed after each cycle with 2 mg/L NaOCl. Before the next cycle begins, DI water was filtered for 3 min to determine the hydraulically irreversible fouling (HIF), and the average transmembrane pressure during the 3 min filtration was used as a measure of the HIF. After determination of the HIF, the module was detached and one fouled hollow fiber was carefully cut off from the module. The fouled membrane specimen was stored in a 22 ml glass vial, in which a piece of wetted paper towel was

kept to maintain humidity and keep the fiber from drying. After sampling, the remaining of the cut membrane fiber was sealed with epoxy and the module was reassembled for the next cycle filtration. For each filtration experiment, a new membrane bundle was potted and mounted in the detachable module. The fouled membrane samples were analyzed for polymer flocculants by Fourier Transform Infrared Spectroscopy (FTIR); this analysis was attempted to verify the hypothesis that the polymer flocculant accumulates on the membrane surface during the filtration process.

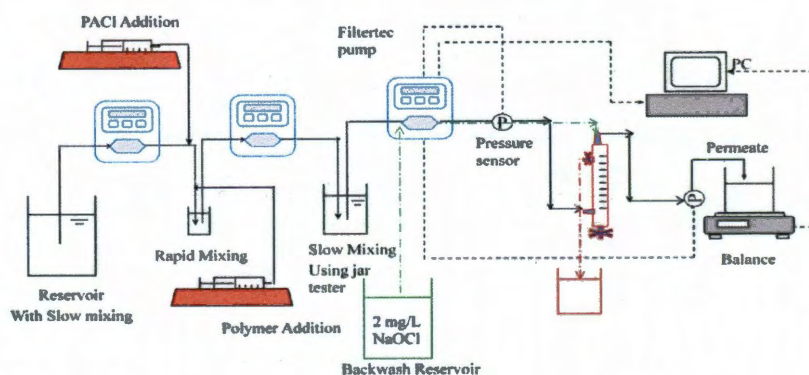


Figure 7-4 Schematic of hollow fiber membrane filtration

### 7.2.7. Scanning Electron Microscopy Protocol

Both surface and cross sectional images of the hollow fiber membrane samples were taken. For the cross sectional image of the hollow fiber membrane sample, the sample was first fractured using liquid nitrogen. The way of liquid nitrogen quench is described as follows: a piece of aluminum foil was placed on a Petri-dish and covered half of the Petri-dish area. The liquid nitrogen was filled into the Petri-dish until its level was higher than the aluminum foil. After the liquid nitrogen on the aluminum foil evaporated (to avoid the bubbling of nitrogen which can possibly destroy the cake layer

on the hollow fibers), the samples were pinched with a pair of tweezers at the end of the fibers to approach the aluminum foil surface. At the close vicinity of the aluminum foil, the fouled membrane was frozen by the low temperature already, which guaranteed the integrity of the cake layer. The frozen membrane samples were then placed on the aluminum foil for at least 20 seconds, and then fractured with two pair of tweezers. For the surface image of the hollow fiber membrane sample, the fibers were directly cut with a pair of scissors.

The cut membrane samples were then treated using a protocol revised from the method of Ensikat and Barthlott (1993). The samples were soaked in the triethylene glycol TEG solutions with ascending concentrations (10%, 20%, 30% ... 100%) for five minutes, the treated samples were then soaked in 100% TEG solution under 4 °C until SEM analysis.

For imaging the surface of the hollow fiber membrane, the fibers were mounted on a vertical SEM sample holder using an iron thread, which is illustrated in Figure 7-5 below. For the cross sectional imaging, the fractured membrane samples were directly amounted onto the vertical sample. A focused beam Quanta 3D SEM (FEI, Oregon) was used with an environmental mode for the imaging. The environmental mode assured the moisture of the samples throughout the analysis.



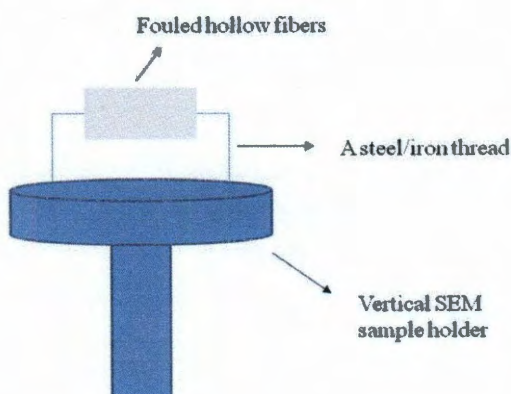


Figure 7-5 Schematic of method for imaging hollow fiber membrane surface

### 7.2.8. Floc Characterization

Coagulation/flocculation experiments were performed for real time analysis of floc size and fractal dimension by static light scattering and small angle light scattering (Jarvis et al., 2008b), respectively, using a Mastersizer (Malvern Mastersizer 2000, Malvern, UK). To avoid floc breakage that the built-in circulation pump may cause, the coagulated water was pumped continuously through the measurement cell of the Mastersizer by a Filtertec peristaltic pump (SciLog, Middleton, WI) installed downstream of the measurement cell. The water was discharged directly after each measurement. The rate of 20 ml/min was used to pump the flocs through the flow cell. A slow mixing time of 680 min was adopted to allow multiple measurements at 30, 90, 180, 300, 450, and 630 min respectively. At least 7 measurements were made at each time point. The extended slow mixing time was intended to match the circulation time used in the following floc attachment efficiency evaluation. Floc size and fractal dimension measurements at this time points help understand the attachment of floc onto membrane surface.



The floc fractal dimension ( $D_f$ ) was determined by linear regression of the scattered light intensity ( $I$ ) as a function of the difference in the wave number between the incident and scattered light ( $Q$ ) (Equations 8-1 and 8-2).

$$I(Q) \propto Q^{-D_f} \quad \text{Eq. 7-1}$$

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad \text{Eq. 7-2}$$

Here,  $n$  is the refractive index of the suspending medium (i.e., water),  $\theta$  is the angle of light scattering ( $0.01$ - $40.6^\circ$ ), and  $\lambda$  is the wavelength of the radiation in vacuum ( $633$  nm).

## 7.3. Results and Discussion

### 7.3.1. Coagulation of Lake Houston Water

Coagulation of Lake Houston water using the 400-500 kDa pDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM was first carried out for dosage optimization, and the results are presented in Figures 7-6 to 7-8. None of the three polymers affected DOC removal significantly. Only the 400-500 kDa pDADMAC increased  $UV_{254}$  removal at low PACl dosages, but the improvement diminished at dosages higher than 15 mg/L. Similar phenomena were observed in the previous part for coagulation of the Mississippi River water and the Grand Lake water. Based on the results, 10 and 0.5 mg/L were selected for PACl and polymer respectively for the following experiments in this part.

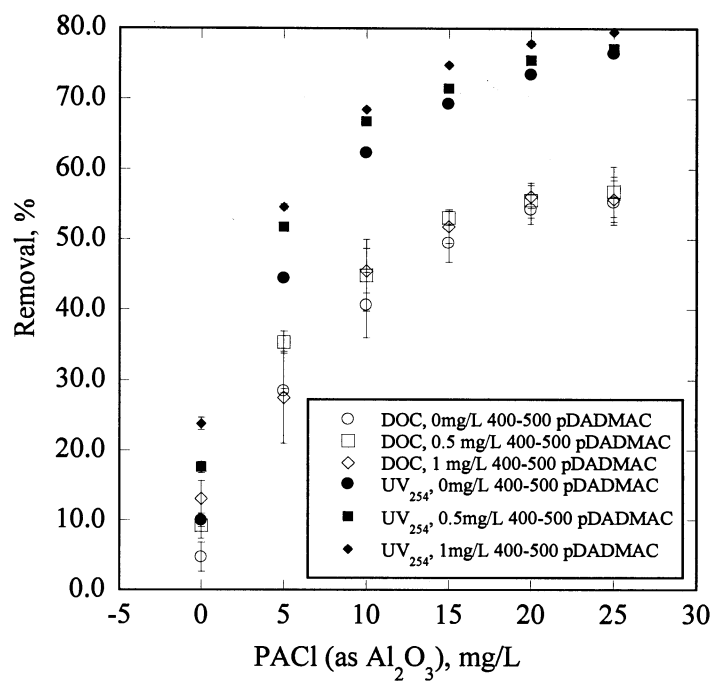


Figure 7-6 DOC and UV<sub>254</sub> removal of Lake Houston water using PACl and 400-500 kDa pDADMAC of various concentrations

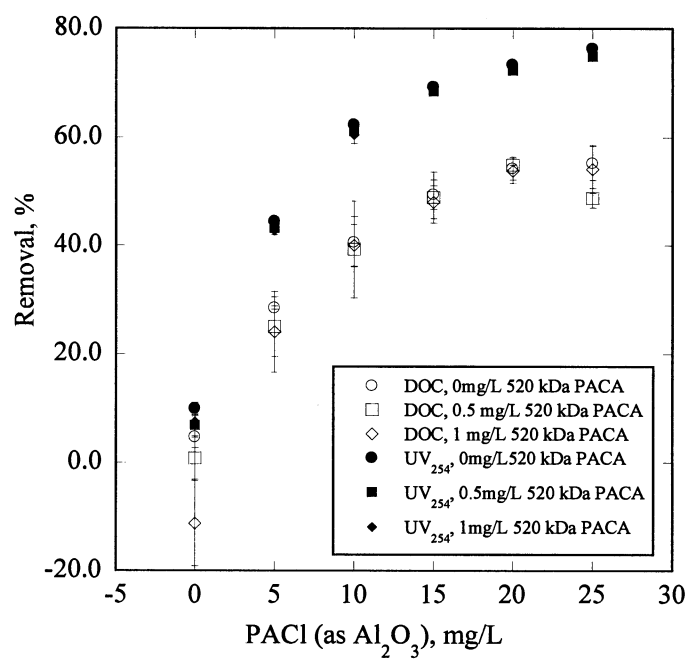


Figure 7-7 DOC and UV<sub>254</sub> removal of Lake Houston water using PACl and 520 kDa PACA of different concentrations

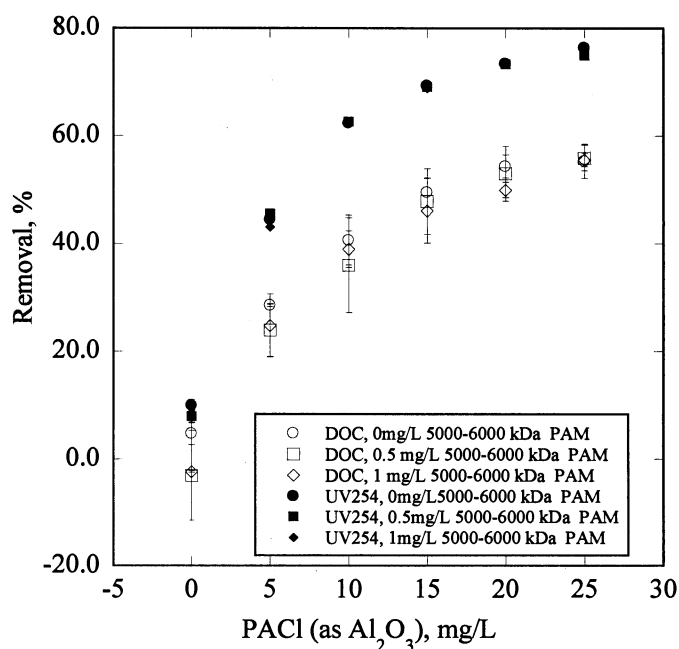


Figure 7-8 DOC and UV<sub>254</sub> removal of Lake Houston water using PACl and 5000-6000 kDa PAM of different concentrations

### 7.3.2. Impact of Polymer Flocculants on Floc Size and Fractal

#### Dimension

According to the optimization result, 10mg/L dosage PACl and 0.5 mg/L polymers were used for the floc size and fractal dimension measurements, and the results are shown in Figure 7-9 and 7-10. As can be seen from Figure 7-9, coagulation of Lake Houston water using PACl only generated flocs of around 280  $\mu\text{m}$  after 30 min's slow mixing. The floc size decreased gradually afterwards and reached a plateau of approximately 200  $\mu\text{m}$  after 300 min slow mixing. The 400-500 kDa pDADMAC increased the floc size to around

450  $\mu\text{m}$  after 30 min slow mixing, and the floc size decreased to about 250  $\mu\text{m}$  after 630 min. The anionic 520 kDa PACA and neutral 5000-6000 kDa PAM increased the floc size much more, with the floc size reaching 380 and 320  $\mu\text{m}$  after 630 min for PACA and PAM respectively. The observed increase of floc size for Lake Houston water by using polymer flocculants is similar to that previously observed with Vinita water and Mississippi River water. The decrease of floc size with extended flocculation time can possibly be attributed to the abrasion by the shear.

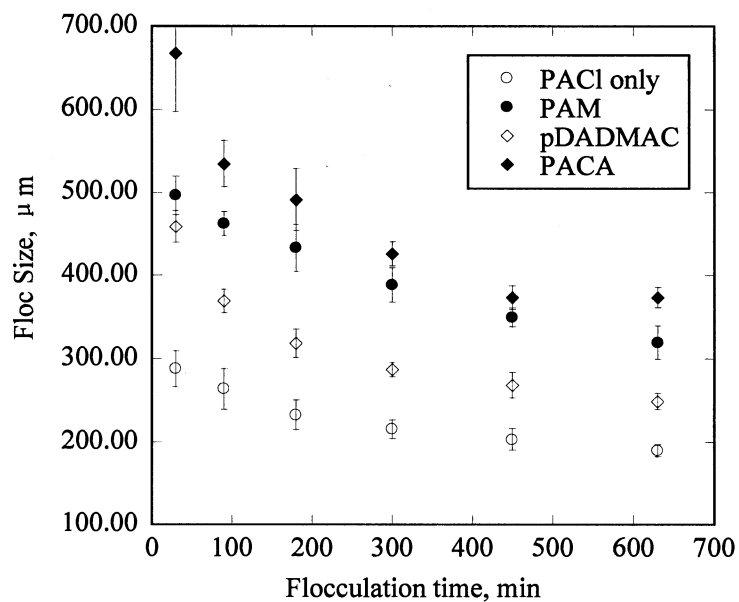


Figure 7-9 Floc size of 10 mg/L PACl and 0.5 mg/L polymers coagulated water at different flocculation time, the polymers used are 5000-6000 kDa PAM, 400-500 kDa pDADMAC, and 520 kDa PACA.

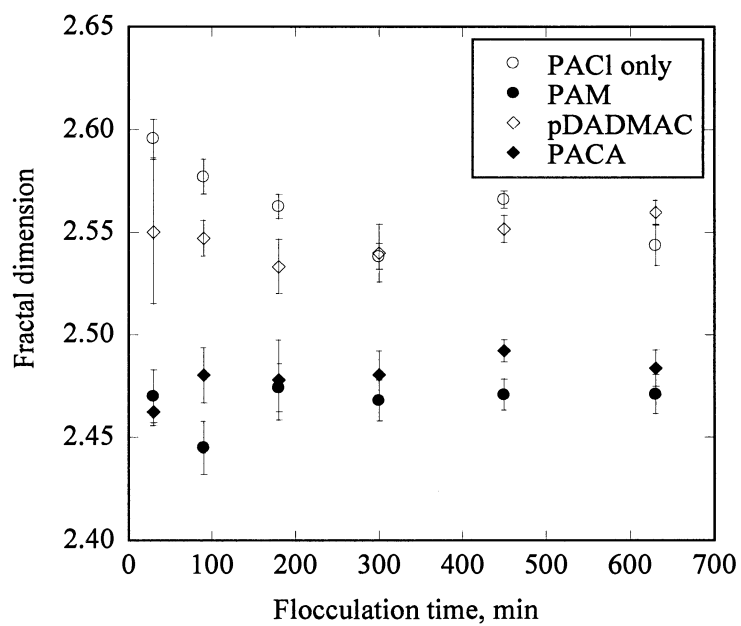


Figure 7-10 Floc fractal dimension of 10 mg/L PACl and 0.5 mg/L polymer coagulated water at different flocculation time, the polymers used are 5000-6000 kDa PAM, 400-500 kDa pDADMAC, and 520 kDa PACA.

Opposite to the increase of floc size, the floc fractal dimensions were decreased by using polymer flocculants as demonstrated in Figure 7-10, which means the flocs became more compact when polymer flocculants were used. The highest fractal dimension value of 2.6 was found for PACl only floc after 30 min's circulation, and the fractal dimension decreased to 2.56 after 630 min's circulation. The use of 400-500 kDa pDADMAC only slightly reduced the floc fractal dimension throughout the 630 min's circulation. The most reductions were brought by using 5000-6000 kDa PAM and 520 kDa PACA, and the fractal dimensions for the two polymers were all between 2.45 and 2.5 throughout the 630 min's circulation. The reason that 400-500 kDa pDADMAC only slightly reduced the floc fractal dimension can be attributed to its positive charges. Possibly, there is electrostatic repulsion between the positively charged pDADMAC molecules and the positively charged PACl species. However, the neutral PAM and the negatively charged PACA were able to produce denser flocs because of the lack of electrostatic repulsion.

### **7.3.3. Impact of Polymer Flocculants on Floc Attachment Efficiency**

#### **7.3.3.1. Attachment of PACl Only Floc on Polymer Coated Membrane**

The mass of attached PACl only flocs on polymer coated membranes are presented in Figure 7-11. As can be seen from the figure, the accumulated floc mass after 120 min of cross-flow filtration was 1.45 mg when no polymer coating was used, but reached 2.1, 2.4, and 2.47 mg when 400-500 kDa pDADMAC, 5000-6000 kDa PAM,

and 520 kDa PACA were used respectively. To determine whether the procedure used to collect floc particles was able to recover all attached particles, the measurement of accumulated floc on PAM pre-loaded membrane were repeated 3 times with 3 min pure water flush at the end of the 120 min filtration. The pure water flush rate was the same as the cross-flow rate used during filtration, but no permeate was drawn during the flush. The flushing using 20 ml/min without drawing permeate has been shown to remove flocs rapidly from the membrane surface in numerous experiment trials. All the flush water was collected and filtered through the same 0.45  $\mu\text{m}$  membrane for floc mass measurement. The average floc mass was 2.35, which was similar to 2.4 and demonstrated that all the accumulated flocs were collected. To identify the contribution of the flocs in the bulk liquid inside the module, the same volume of flocculated water after 20 min's slow mixing but before circulation was filtered. The mass (about 0.4 mg) was much lower than that under any other condition as shown in Figure 7-11, which confirmed that there was indeed an accumulation of flocs on membrane surface.

The significantly increased floc attachment by anionic PACA can be explained as follows: since the PVDF membrane is negatively charged (Wang et al., 2011), when the negatively charged PACA was coated onto the negatively charged membrane surface, it is possible that most of the PACA molecules stood up on the negatively membrane surface because of electrostatic repulsion. Because the PAM is neutral and has much higher molecular weight, they might have random conformations on membrane surface, which can help retain floc on membrane surface to a certain degree. The situation was completely different for positively charged pDADMAC molecules. They tend to stick on the membrane surface and have much lower impact on the floc attachment efficiency.



Therefore, the average accumulated floc mass was slightly less than both PACA and PAM, and statistical analysis indicated that the difference is significant at 90% confidence level. The hypothesized confirmations of different polymers on membrane surface are depicted in Figure 7-12.

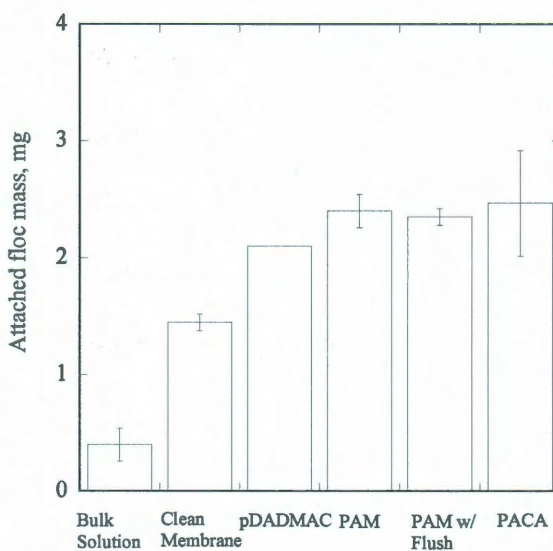


Figure 7-11 Floc mass using different PACI and polymer concentrations

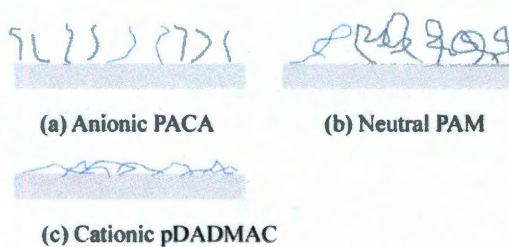


Figure 7-12 Hypothesized molecular confirmation of different polymers on negatively charged PVDF membrane surface

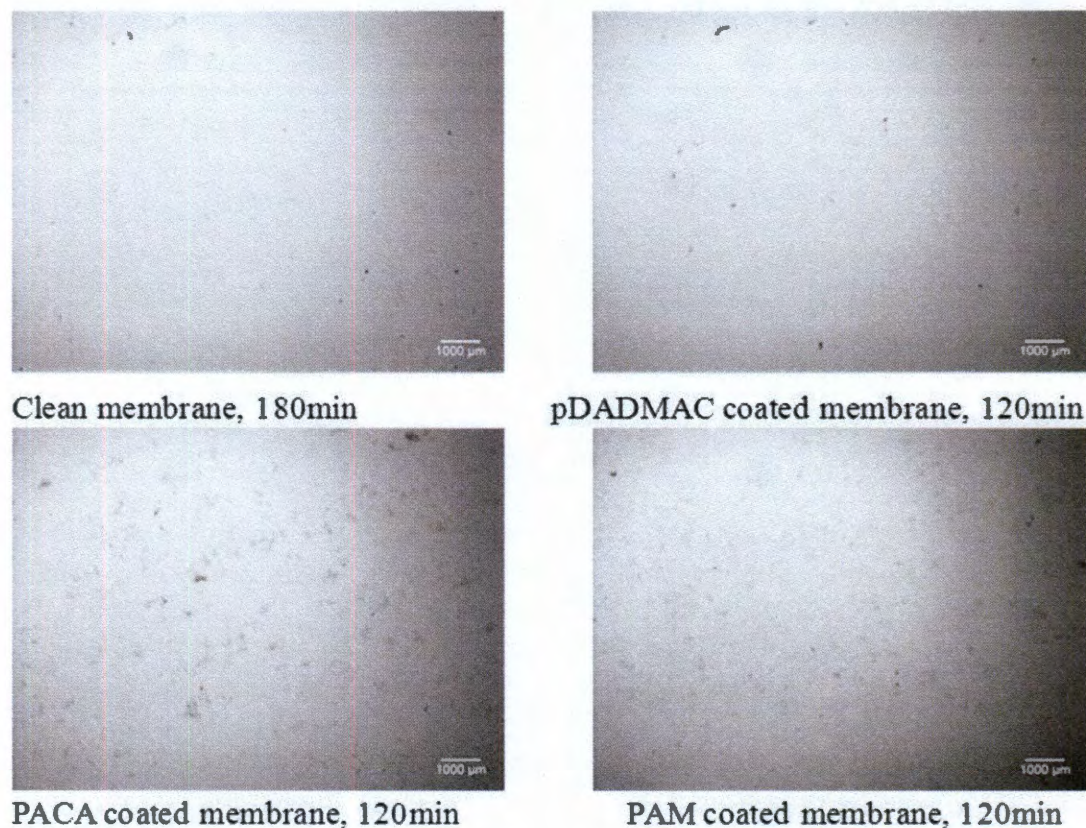


Figure 7-13 Microscope images of dried membrane after circulation of PACl only floc: (a) clean membrane after 180 min's circulation; (b) pDADMAC coated membrane after 120 min's circulation; (c) PACA coated membrane after 120 min's circulation; (d) PAM coated membrane after 120 min's circulation

The dried membranes after circulation were subjected to microscopic observation. The results are shown in Figure 7-13. It is obvious that there are only a tiny amount of flocs left on the membrane surface for clean and pDADMAC coated membranes, but significantly more flocs remained on PACA and PAM coated membranes, which again demonstrated that polymer especially anionic and neutral PAM can increase floc attachment efficiency.

### 7.3.3.2. Attachment of Polymer Pre-incorporated Floc on Clean Membrane

The attachment of floc particles formed in the presence and absence of a polymer flocculant on clean membranes is presented in Figure 7-14. The data clearly show faster deposition of floc particles formed in the presence of a polymer flocculant. PACl only floc reached a cumulative floc mass of 6.6 mg after 630 min of filtration. The cationic pDADMAC increased the floc mass to 10.1 mg while both neutral PAM and anionic PACA increased the floc mass to 8.9 mg. In the size range of the floc particles, shear induced diffusion and inertial lift are two dominant mechanisms of particle transport in cross-flow filtration. Since the permeate flux and cross-flow velocity were kept constant in all experiments, transport of floc particles formed in the presence of a polymer flocculant is expected to be less than those formed with PACl alone because of their larger particle size and consequently faster back transport due to greater shear induced diffusion and inertial lift. The increased floc accumulation on the membrane surface suggests that floc particles formed in the presence of a polymer flocculant have greater attachment efficiency to the membrane surface. This could be attributed to two factors: 1) Polymer molecules on the floc particle surface enhance attachment of floc particles to the membrane. This effect can be clearly seen in the highest accumulation rate of floc formed with pDADMAC, whose positive charges render strong electrostatic attraction with the negatively charged membrane surface. 2) The more fractal structure of the floc particles formed in the presence of a polymer flocculant provides more contact points for floc attachment.

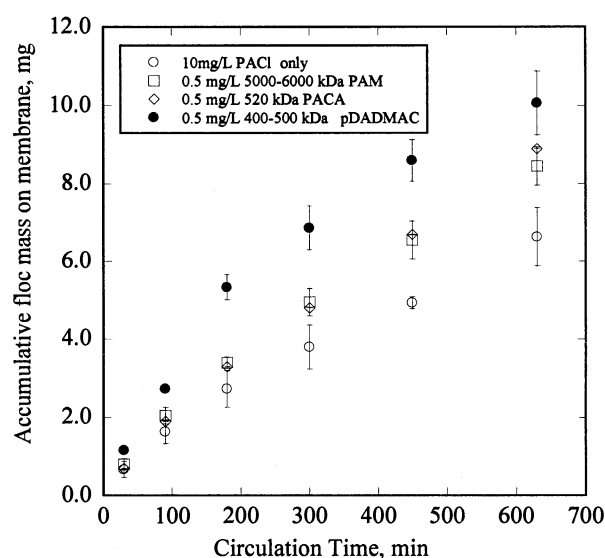


Figure 7-14 Cumulative mass of attached floc using different PACl and polymer concentrations

### 7.3.3.3. Filming of Floc Attachment onto Membrane Surface

The depositions of flocs onto the membrane surface were filmed under two conditions: flocs with/without polymer flocculants onto clean membrane surface and PACl only flocs onto polymer coated membranes. Because the extreme large size of the videos, they will be presented in a separate storage disk.

According to the videos taken for various conditions, the flocs with polymer flocculants deposited onto the clean membrane surface faster than those without polymers. Moreover, the deposition rate of floc particles formed with pDADMAC was much higher than those formed with PAM or PACA, while the rates were similar between PAM and PACA. Again, the difference can possibly be attributed to different electrostatic interactions between flocs with different polymers and membrane surface.



With positively charged pDADMAC, there might be electrostatic attraction between the flocs and membrane surface, but there might be electrostatic repulsion or no interaction for flocs with negatively charged PACA and neutral PAM. For deposition of PACl only flocs onto polymer coated membrane surface, slow attachment of PACl only floc onto pDADMAC coated membrane was observed, and very fast attachment of PACl only flocs onto PACA and PAM coated membranes. The final attachment amount of flocs on pDADMAC coated membranes appeared much less than the PACA and PAM coated membrane. This is expected and consistent with the mass measurement result. However, no obvious difference in deposition rate of PACl only flocs was observed between clean and pDADMAC coated membrane surface. The result further demonstrated the importance of the steric effect of the polymers in the system as shown in Figure 7-12.

#### **7.3.4. Impact of Polymer Flocculants on Foulant Layer Characteristics (Structure and organic content change)**

##### **7.3.4.1. Filtration using the detachable module**

The membrane fouling profiles by using different polymer flocculants are presented in Figure 7-15; 10 mg/L PACl and 0.5 mg/L polymer flocculants were used for the filtrations. As can be seen from Figure 7-15, all three polymers significantly increased membrane fouling at the end of the fifth filtration cycle compared to when PACl alone was used. The neutral, high molecular weight PAM caused the most fouling, and the anionic PACA was the least detrimental among the three polymer types tested. The hydraulic irreversible fouling for each condition is also presented in Figure 7-15. All the three polymer flocculants increased the hydraulically irreversible fouling (HIF). After five

filtration cycles, the pDADMAC caused more HIF than both PAM and PACA, but PAM and PACA resulted in similar HIF. The higher membrane fouling and higher HIF caused indicated that polymers make the cake layer either denser or stickier.

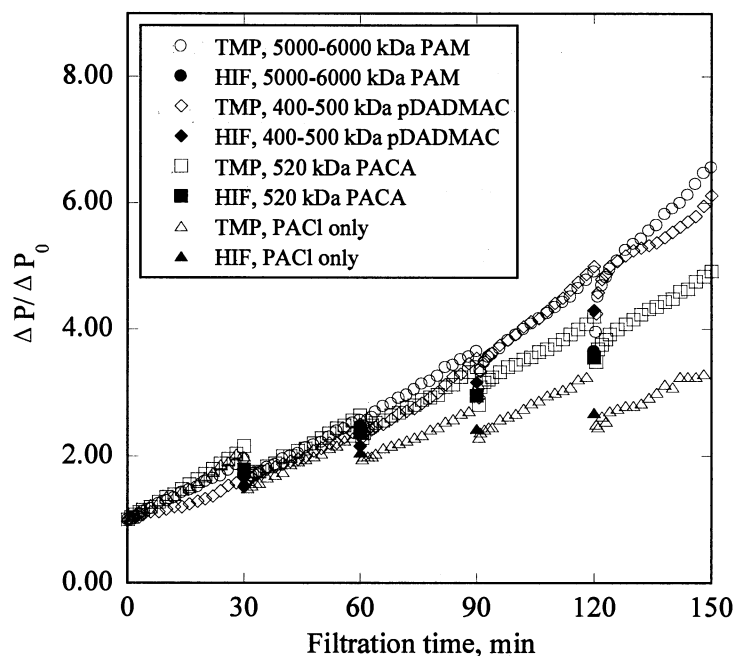


Figure 7-15 Membrane fouling by using different polymer flocculants, the dosages for PACI and Polymer flocculants were 10 and 0.5 mg/L respectively.

#### 7.3.4.2. Impact of Polymer Flocculants on Foulant Layer Structure

SEM images of clean and fouled membranes were taken to characterize the cake layer with different polymer flocculants. The results are presented in Figures 7-16 to 7-20. Totally five conditions were tested: clean membrane, 10 mg/L PACI only, 10 mg/L PACI only and 0.5 mg/L 520 kDa PACA, 10 mg/L PACI only and 0.5 mg/L 5000-6000 kDa PAM, and 10 mg/L PACI only and 0.5 mg/L 400-500 kDa pDADMAC. For each

condition, both cross section and surface of the hollow fibers were imaged. However, by this method, no obvious difference in the cake layer structure can be observed between different conditions. This might be caused by the pretreatment method used: wetting using triethylene glycol. Another pretreatment method using resin embedding has been prepared for SEM imaging to confirm the phenomenon; the result will be updated before the final submission of this dissertation.

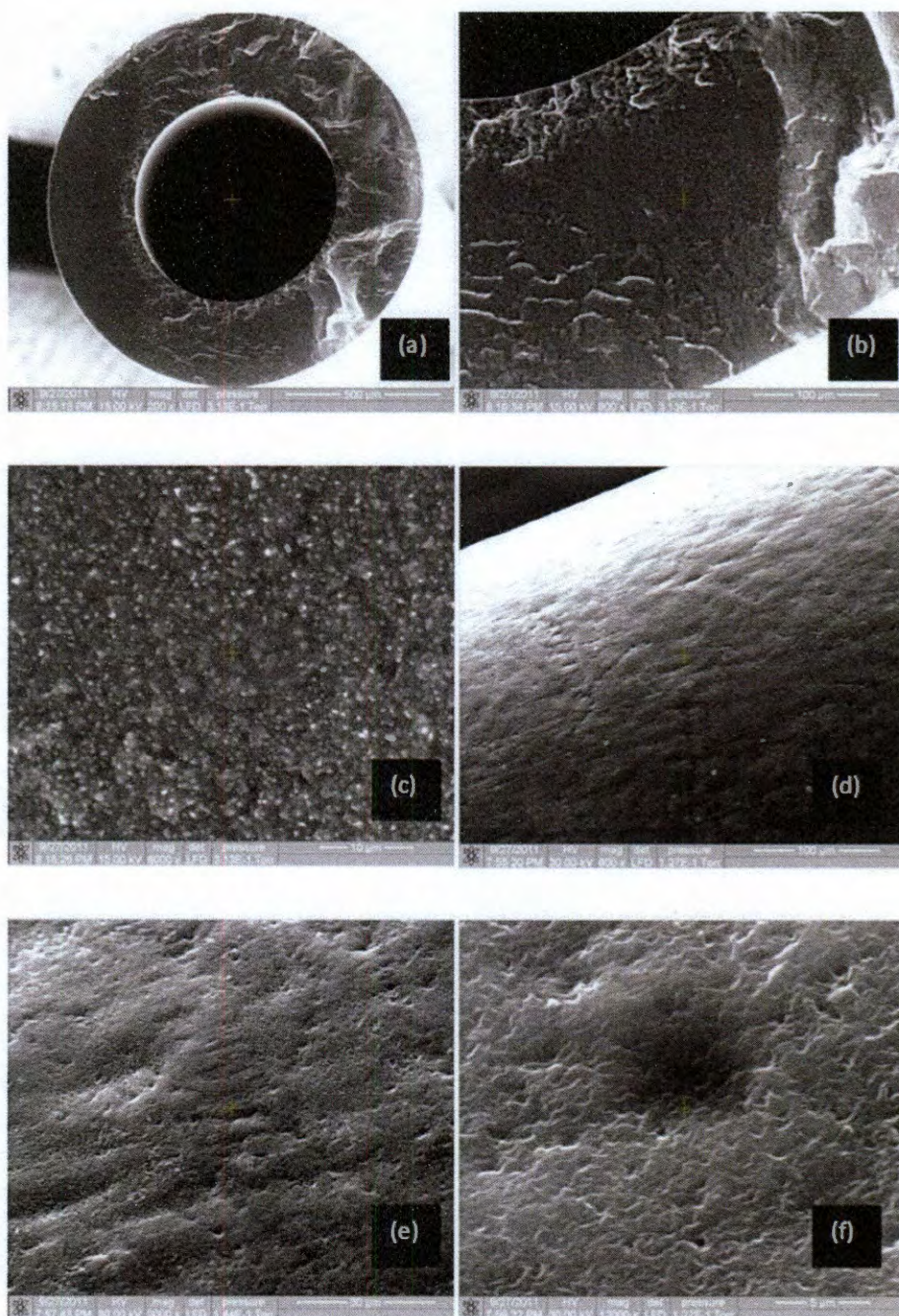


Figure 7-16 SEM images of clean membranes: a, b, and c are cross sectional images; d, e, and f are surface images.



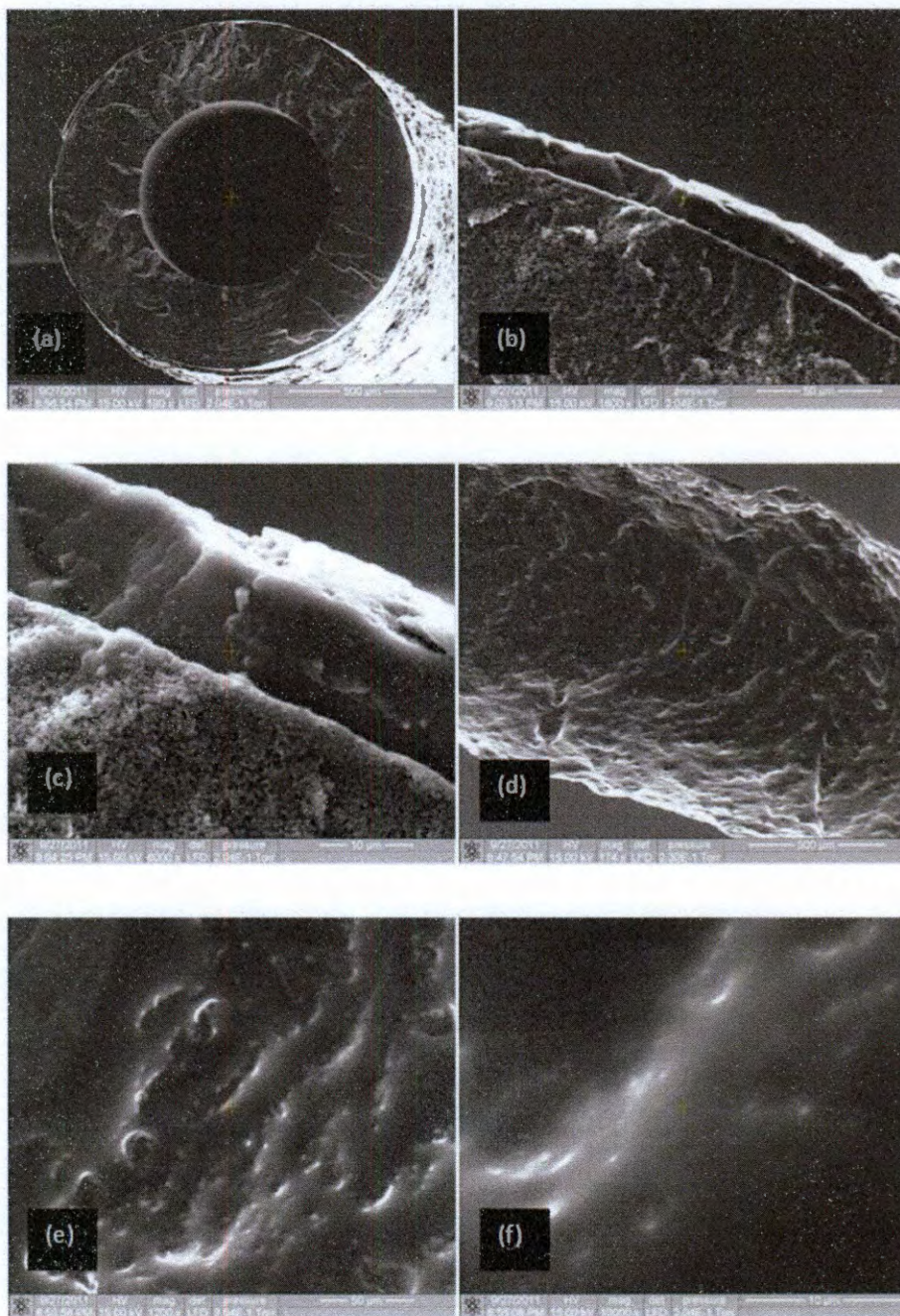


Figure 7-17 SEM images of PACl only flocs fouled membrane: a, b, and c are cross sectional images; d, e, and f are surface images.



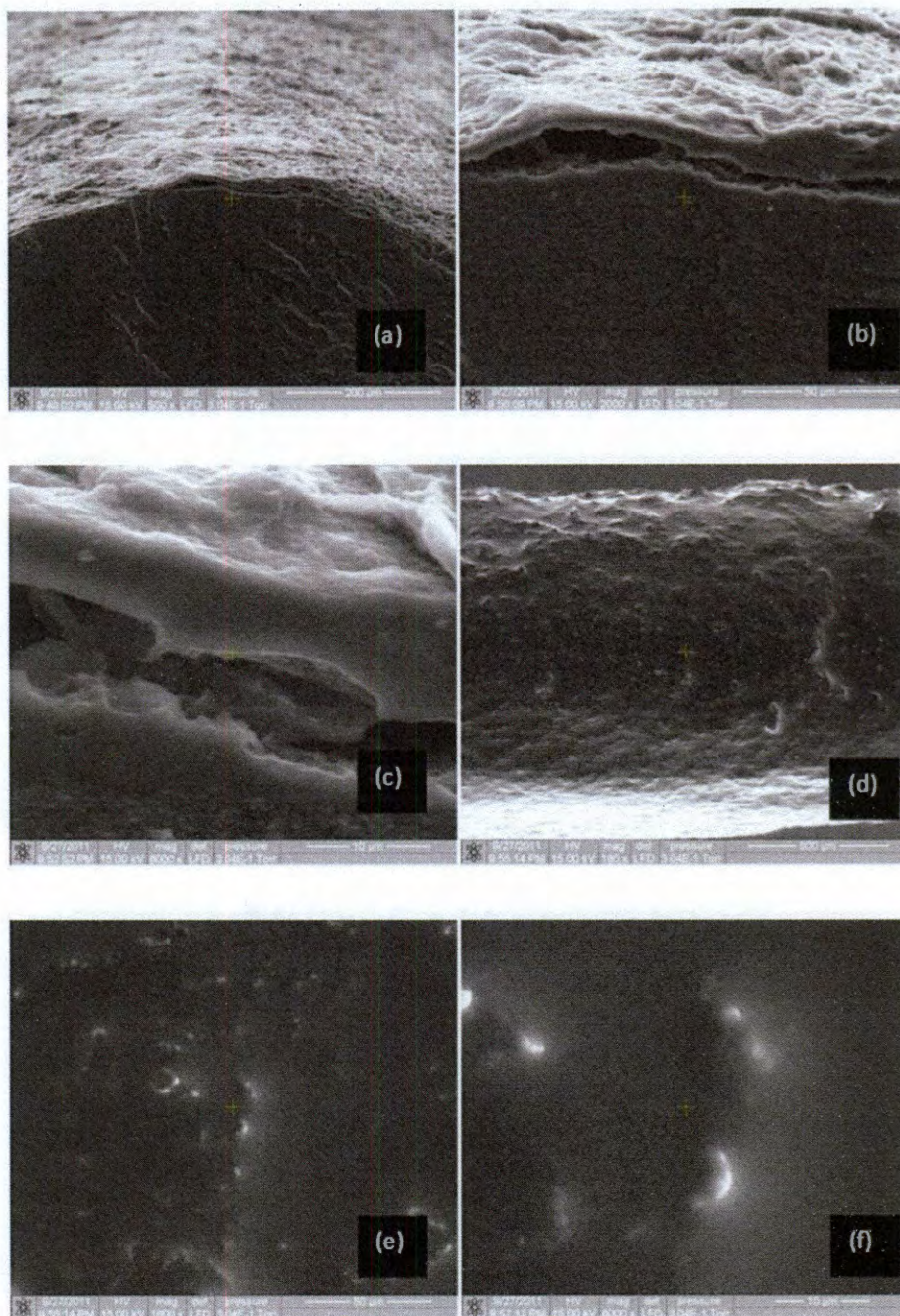


Figure 7-18 SEM images of PACA floccs fouled membrane: a, b, and c are cross sectional images; d, e, and f are surface images.



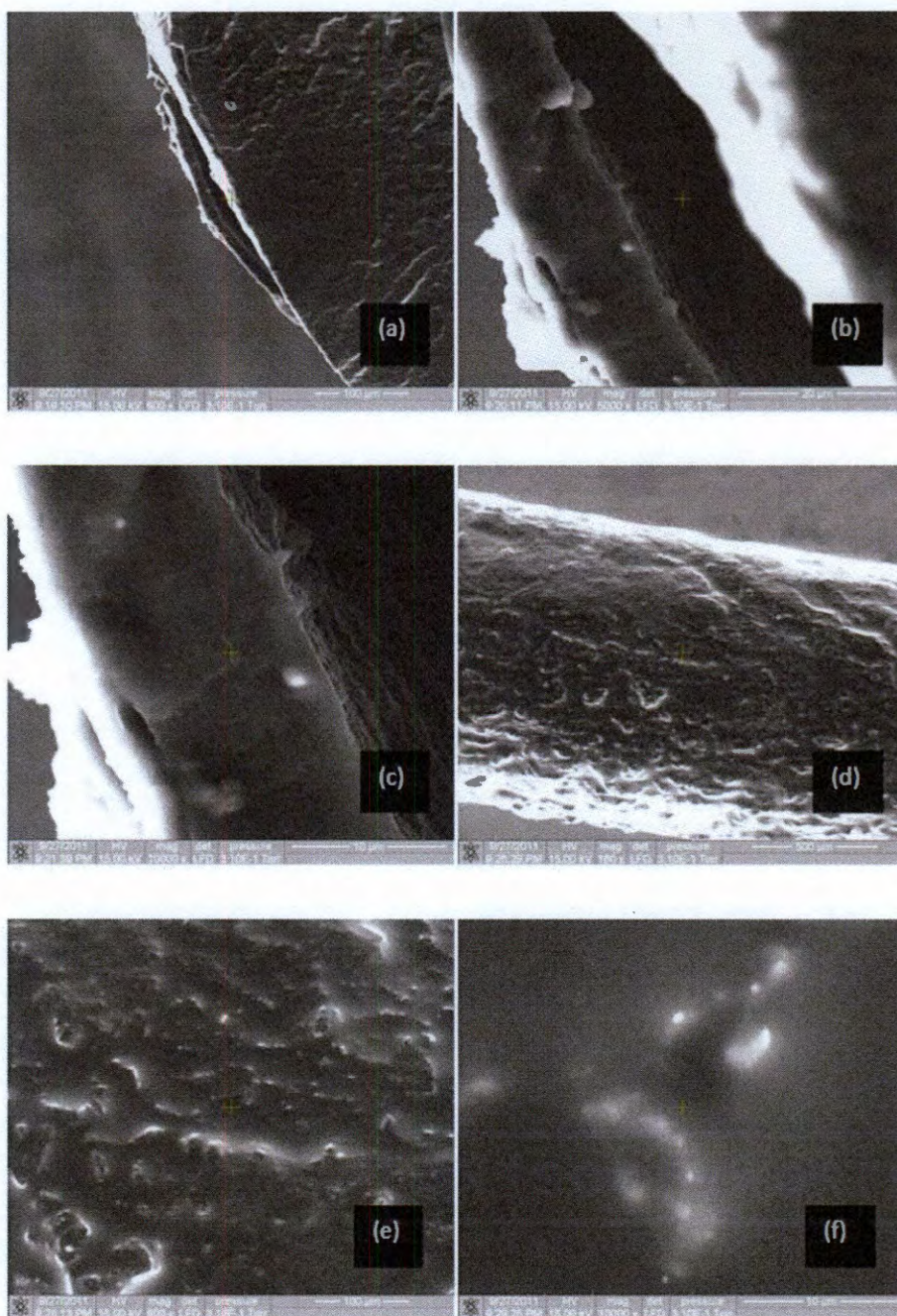


Figure 7-19 SEM images of PAM flocs fouled membrane. a, b, and c are cross sectional images; d, e, and f are surface images



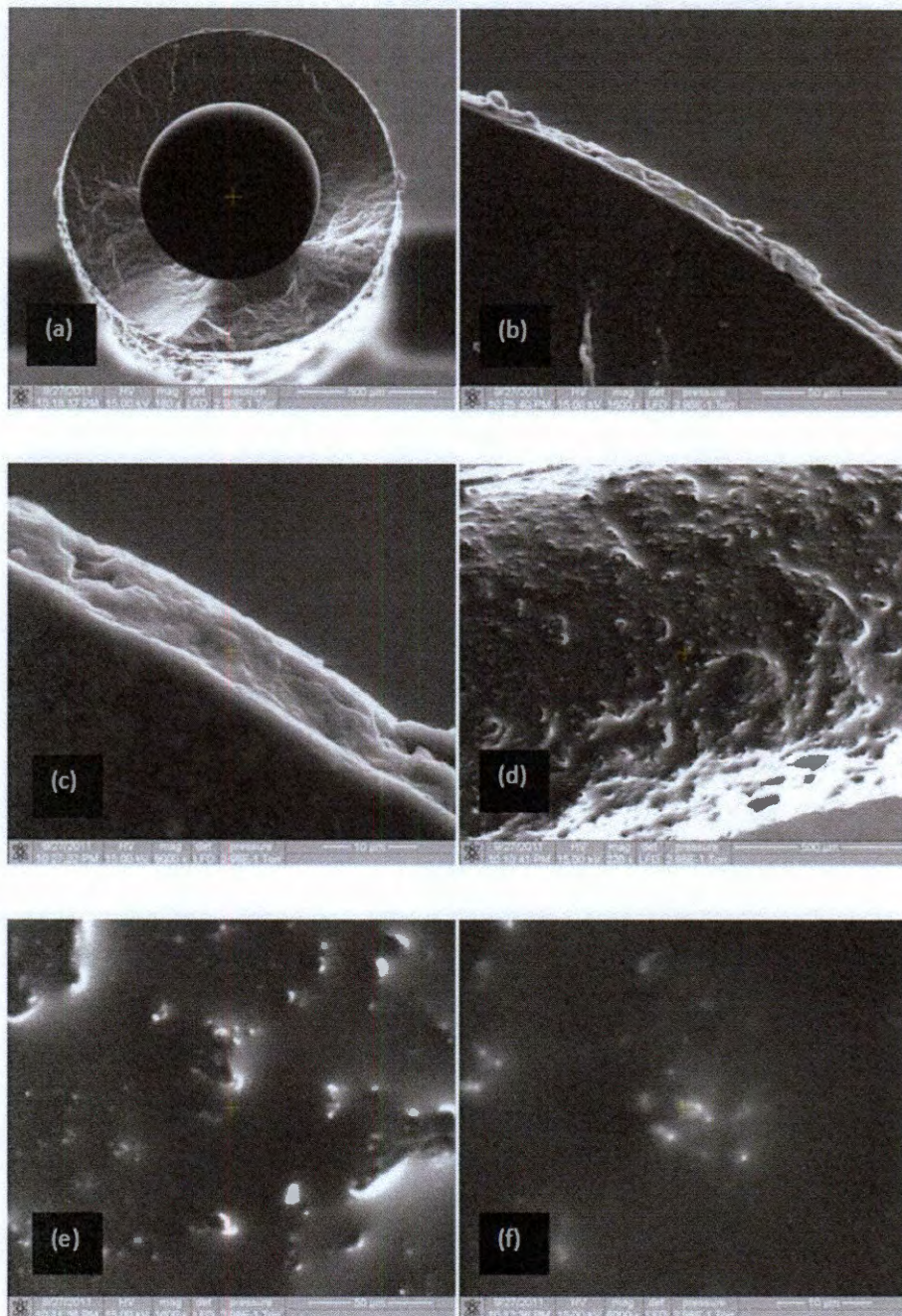


Figure 7-20 SEM images of PAM flocs fouled membrane: a, b, and c are cross sectional images; d, e, and f are surface images.

#### **7.3.4.3. Impact of Polymer Flocculant on Organic Content Change of Foulant Layer**

Pure polymer, clean membrane, and fouled membranes were analyzed by ATR-FTIR. The results are presented in Figures 7-21 to 7-26. Figures 7-23 to 7-25 clearly show that the concentration of natural organic matter on the membrane surface increased with the filtration cycles. Physical scraping of the fouled membranes using Kim wipes was performed aiming at identifying polymer flocculants under cake layer. The physical cleaning removed all the visible foulant, but it was not able to eliminate the organic foulants on the membrane surface as demonstrated by the significant residual FTIR signal. This is consistent with the significant irreversible fouling shown in Figure 7-15. As shown in Figure 7-26, there was notable more NOM foulant on the membrane when a polymer flocculant was used in conjunction with PACl.

The ATR-FTIR analysis of the fouled membrane samples was not able to identify the presence of polymer flocculants on the fouled membrane surface, as shown by the similar spectra obtained with different polymers in Figure 7-26. This should be attributed to two reasons: (1), the NOM content in the cake layer is much higher than the polymer flocculants, which induced significant interference for polymer detection; (2), the ATR-FTIR technology itself cannot provide sufficient low detection limit. Therefore, future research should concentrate on pretreatment of the cake layer to separate polymer flocculants and explore techniques with lower polymer detection limit.

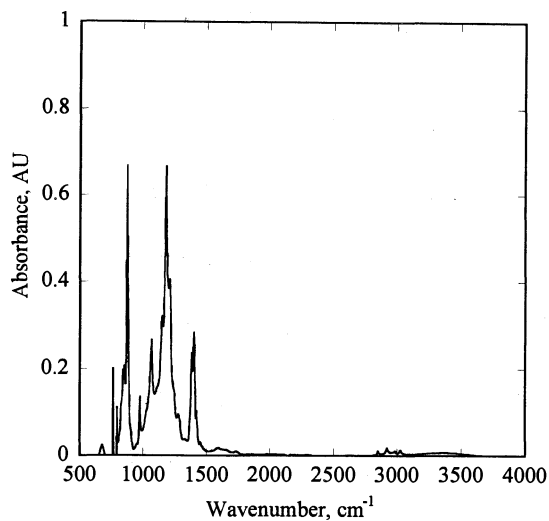


Figure 7-21 ATR-FTIR spectrum of clean PVDF membrane

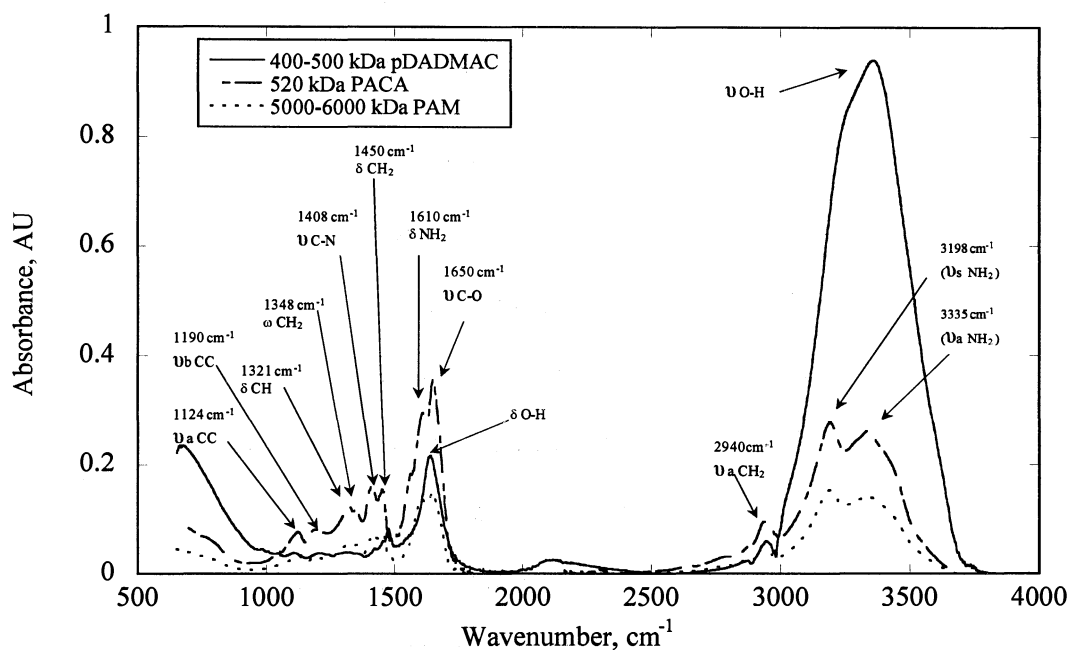


Figure 7-22 ATR-FTIR spectrum of pure 400-500 kDa pDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM. The spectrum of 400-500 kDa pDADMAC is similar to that of pure water, because the raw 400-500 kDa pDADMAC reagent is 20% in water.

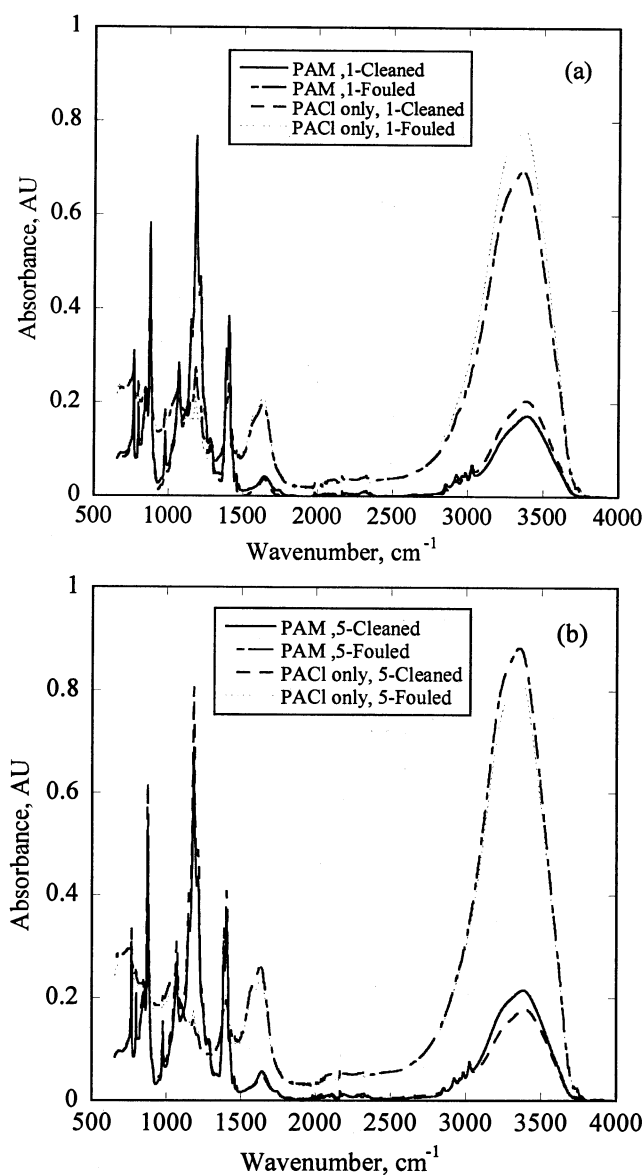


Figure 7-23 ATR-FTIR spectrum of 5000-6000 kDa PAM fouled membrane. 1-cleaned means physically cleaned membrane after first filtration cycle, 1-fouled means intact fouled membrane after first filtration cycle; 5-cleaned means physically cleaned membrane after fifth filtration cycle, 5-fouled means intact fouled membrane after fifth filtration cycle. The dosages for PACl and Polymer flocculants were 10 and 0.5 mg/L respectively.

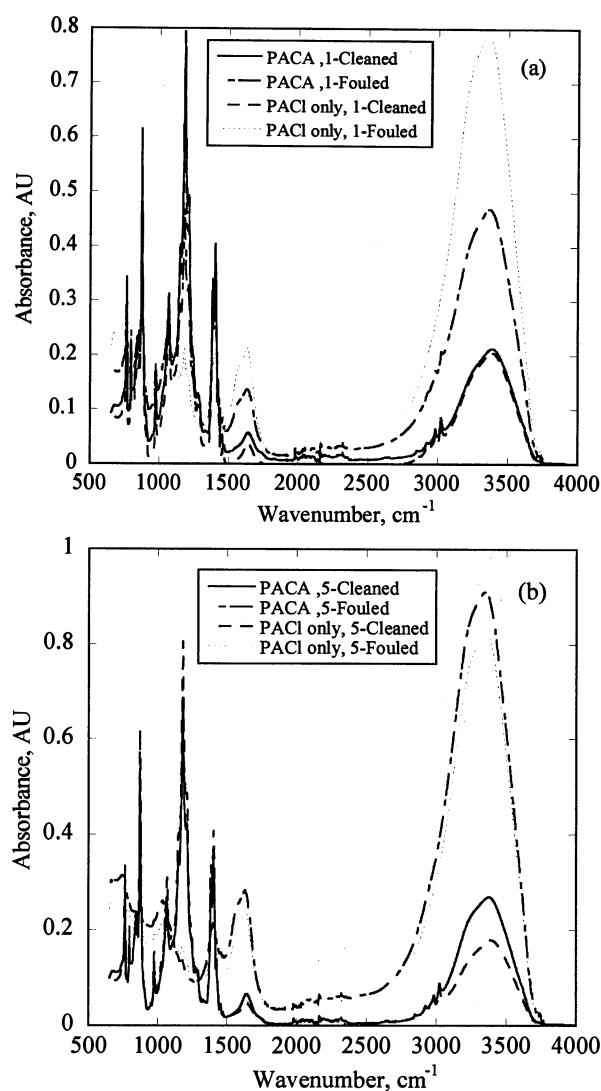


Figure 7-24 ATR-FTIR spectrum of 520 kDa PACA fouled membrane. 1-cleaned means physically cleaned membrane after first filtration cycle, 1-fouled means intact fouled membrane after first filtration cycle; 5-cleaned means physically cleaned membrane after fifth filtration cycle, 5-fouled means intact fouled membrane after fifth filtration cycle. The dosages for PACl and Polymer flocculants were 10 and 0.5 mg/L respectively.



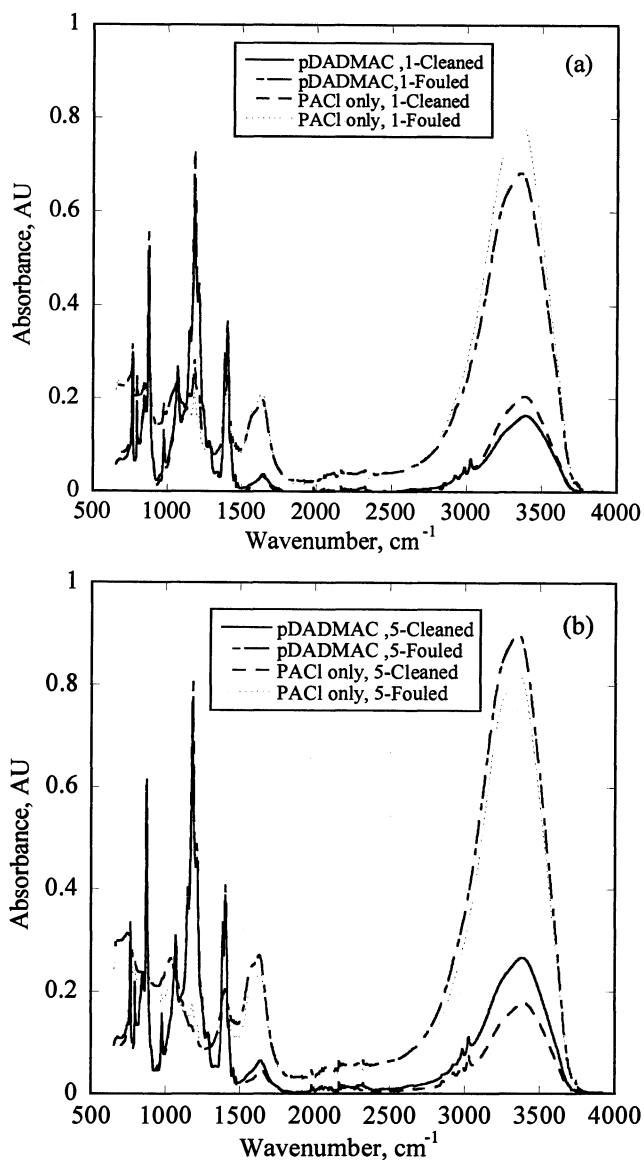


Figure 7-25 ATR-FTIR spectrum of 400-500 kDa pDADMAC fouled membrane. 1-cleaned means physically cleaned membrane after first filtration cycle, 1-fouled means intact fouled membrane after first filtration cycle; 5-cleaned means physically cleaned membrane after fifth filtration cycle, 5-fouled means intact fouled membrane after fifth filtration cycle. The dosages for PACl and Polymer flocculants were 10 and 0.5 mg/L respectively.

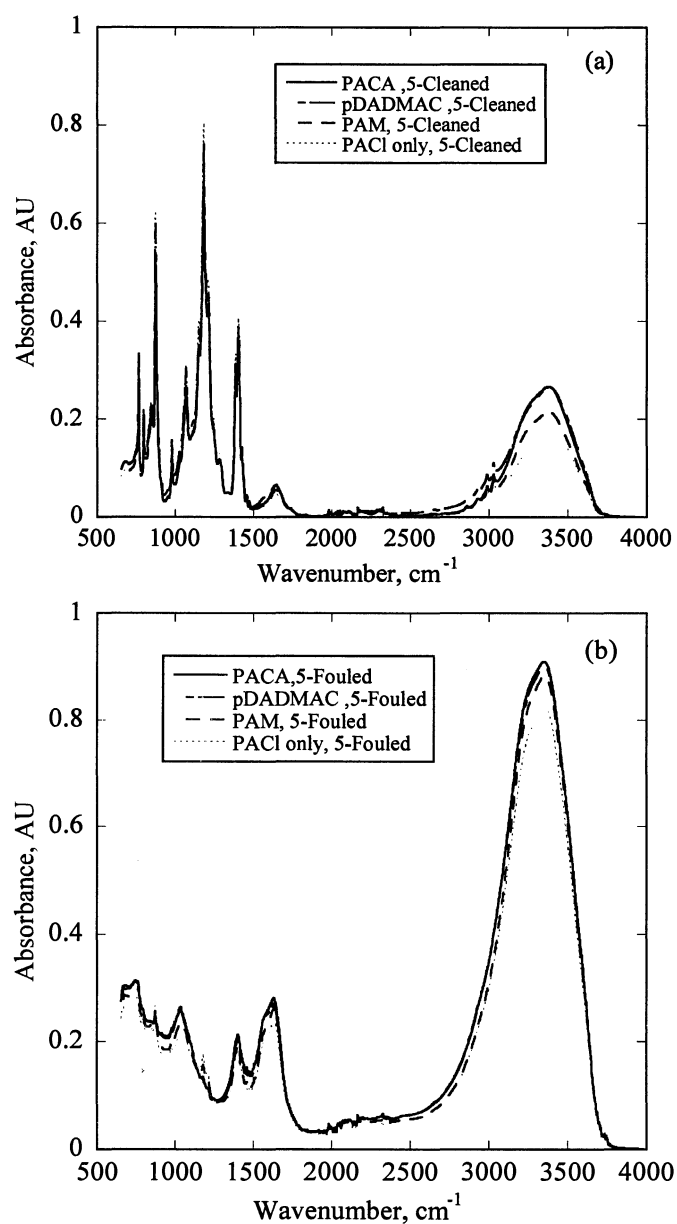


Figure 7-26 Membrane fouling by using different polymer flocculants. 1-cleaned means physically cleaned membrane after first filtration cycle, 1-fouled means intact fouled membrane after first filtration cycle; 5-cleaned means physically cleaned membrane after fifth filtration cycle, 5-fouled means intact fouled membrane after fifth filtration cycle. The dosages for PACl and Polymer flocculants were 10 and 0.5 mg/L respectively.

## 7.4. Conclusions

The impact of polymer flocculants on floc attachment efficiency was evaluated using 400-500 kDa pDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM. All the three polymer flocculants increased floc size but decreased floc fractal dimension. The neutral PAM and anionic PACA resulted in larger floc sizes and smaller fractal dimension than the cationic pDADMAC. The three polymer flocculants significantly increased the attachment efficiency of floc particles onto both the clean and polymer flocculant fouled MF membrane. On the clean membrane surface, the cationic pDADMAC resulted in higher accumulated floc mass than the neutral PAM and anionic PACA, and the foulant masses attached when using PAM or PACA were similar. The deposition rate of floc particles formed with pDADMAC was also much higher than those formed with PAM or PACA. On polymer flocculant fouled membrane surfaces, however, the relative impact of the polymer flocculants on floc attachment efficiency was reversed. Although the accumulation of foulant mass attached when PAM or PACA was used was still similar, it was much greater than that when pDADMAC was used. The increase of floc attachment efficiency on MF membrane partially explains the increased membrane fouling by using polymer flocculants in our previous study.

## ***Chapter 8 Conclusions***

## **8.1. Fouling of Microfiltration Membranes by Organic**

### **Polymer Coagulants and Flocculants**

In this section, membrane fouling by free polymer flocculants was studied. Synthetic water containing only polymer flocculants and background salts were filtered through flat-sheet membranes under different pH conditions. This study demonstrates that carry-over of polymers used in the coagulation/flocculation pretreatment can cause severe fouling of MF membranes even at very low concentrations. MF membrane fouling by polymers strongly depends on the molecular weight, charge, and concentration of the polymer, as well as the membrane surface properties. Cationic polymers tend to cause greater fouling than anionic and nonionic polymers in synthetic feed water due to the strong electrostatic attraction between the positively charged polymer and the negatively charged membrane surface. Among polymers of the same charge, those with higher molecule weight have greater fouling potential. Although changes in electrostatic interaction due to changes in either pH or calcium concentration did not have much impact on MF fouling, pH or calcium concentration can affect fouling by mediating specific foulant-foulant or foulant-membrane interactions. In spite of the small size of the polymers relative to the size of MF membrane pores, surface pore blockage was found to be the predominant fouling mechanism. Formation of large aggregates on the membrane surface suggests that prediction of fouling mechanisms based on foulant molecular size and membrane pore size can be erroneous sometimes. Membrane surface chemical and physical heterogeneity and specific membrane-foulant interactions may be more important than the physical screening mechanism.

## **8.2. Impact of Polymer Flocculants on Microfiltration of Surface Water — Part I: Coagulation Pretreatment**

The impact of polymer flocculants on contaminant removal in the coagulation process was studied in this section. The impact of polymer flocculants on floc properties was also investigated partially in this section. The results showed that none of the polymer flocculants used evidently increased turbidity removal when microfiltration was used. The impact of polymer flocculants on NOM removal strongly depends on the water quality and the molecular characteristics of the polymer. For low DOC waters, none of the polymer flocculants tested was able to improve NOM removal; over-dosage of the polymer actually led to increase in DOC concentration due to significant residual of the polymer in filtered water. Some improvement in NOM removal was found for a high DOC water, but different polymers seems to remove different NOM fractions. Only the cationic pDADMACs removed UV absorbing NOM, likely through charge neutralization. HPSEC Analyses show that residual NOM molecules after PACl coagulation are all in the low molecular weight range ( $<4000$  Da). The cationic pDADMAC enhanced removal of NOM in MW range of 1100-4000 Da. The smaller NOM molecules were not affected. The use of polymer flocculants has a great impact on floc size and structure. Increasing the polymer/PACl ratio results in larger, looser and more open floc particles, which should bring about lower specific cake layer resistance according to Lee et al. (2005) and Park et al. (2006). These findings suggest that the use of polymer flocculants, especially cationic polymers, has some benefit in treating high

DOC surface waters of level; their use for low DOC waters, however, should be evaluated carefully.

### **8.3. Impact of Polymer Flocculants on Microfiltration of Surface Water — Part II: Membrane Filtration**

The effect of polymer flocculants on membrane fouling in the coagulation-microfiltration system was systematically evaluated under various conditions. Polymers were found to worsen membrane fouling under most conditions, even though they may bring slight benefit for NOM removal. Only the pDADMACs reduced membrane fouling for filtrations with sedimentation. The main factor controlling membrane fouling is attributed to the residual colloidal NOM. In the direct mode hollow fiber filtration, hydraulically irreversible fouling was found to affect membrane fouling the most probably due to the accumulation of polymers on the membrane surface; membrane fouling is highly affected by polymer/PACl ratio. With higher PACl dosage, higher membrane fouling can be caused by more solid generated from higher PACl dosage. With lower PACl dosage, higher membrane fouling can be caused by higher hydraulically irreversible fouling due to more exposure of membrane surface to polymers. The membrane fouling was found to be higher with increased floc size and reduced floc fractal dimension, which is contrary to the result of Lee et al. (2005) and Park et al. (2006).

## **8.4. Impact of Polymer Flocculants on Floc Properties and Cake Layer Structure**

The impact of polymer flocculants on floc properties (primarily stickiness) and cake layer structure was studied in this section. Three polymer flocculants were used: 400-500 kDa pDADMAC, 520 kDa PACA, and 5000-6000 kDa PAM. Two membrane reactors were designed for this investigation: a cross flow flat sheet membrane reactor and a detachable hollow fiber membrane reactor. With the cross flow flat sheet membrane reactor, the impact of polymer flocculants on floc stickiness was evaluated by circulating the coagulated water through the reactor under two conditions: attachment of flocs generated by primary coagulant (PACl) only onto polymer coated flat sheet membrane and attachment of flocs generated from both primary coagulant and polymer flocculants onto clean membrane surface. Measurement of mass of flocs accumulated on membrane surface, imaging of fouled membrane surface, and filming of membrane fouling by flocs under conditions with/without polymer flocculants were carried out.

All the three polymer flocculants increased floc size but decreased floc fractal dimension. The neutral PAM and anionic PACA resulted in larger floc sizes and smaller fractal dimension than the cationic pDADMAC. The three polymer flocculants significantly increased the attachment efficiency of floc particles onto both the clean and polymer flocculant fouled MF membrane. On the clean membrane surface, the cationic pDADMAC resulted in higher accumulated floc mass than the neutral PAM and anionic PACA, and the foulant mass attached when using PAM or PACA were similar. The deposition rate of floc particles formed with pDADMAC was also much higher than



those formed with PAM or PACA. On polymer flocculant fouled membrane surfaces, however, the relative impact of the polymer flocculants on floc attachment efficiency was reversed. Although the accumulation of foulant mass attached when using PAM or PACA was still similar, it was much greater than that when pDADMAC was used. The rates of floc deposition onto PAM and PACA coated membrane surface were much higher than onto pDADMAC coated membrane surface. However, no obvious difference in deposition rate of PACl only flocs was observed between clean and pDADMAC coated membrane surface. The result demonstrated the importance of electrostatic and steric effects during the floc attachment onto membrane surface when polymer flocculants are used.

With a special pretreatment, the wet foulant layers formed by flocs with/without polymers were successfully imaged using the SEM technique. However, no obvious difference was observed. In addition, the ATR-FTIR technique employed was unable to distinguish the polymer flocculants in the foulant layer under the tested conditions.

## ***Chapter 9 Future Research***

The current research systematically investigated the impact of polymer flocculants on coagulation-microfiltration of surface water including both performance and mechanism. Efforts have been undertaken to understand the mechanism of polymer flocculants' impact on the coagulation-microfiltration system. However, several questions remain unclear: (1) What is the concentration of residual polymer flocculants in a normal coagulation/microfiltration system? (2) Will polymer flocculants accumulate in the foulant layer? (3) How is cake layer changed when polymer flocculants are used?

Consequently, to complete the understanding of the impact of polymer flocculants on coagulation-microfiltration of surface water, the future research should continue on developing methods to determine the concentration of both residual polymer flocculants in a coagulated system and polymer flocculants in a cake layer. In addition, a better technique needs to be developed to evaluate the cake layer structure.

## List of References

- Abadi, S.R.H., Sebzari, M.R., Hemati, M., Rekabdar, F. and Mohammadi, T. Ceramic membrane performance in microfiltration of oily wastewater. *Desalination* 265(1-3), 222-228.
- Agoudjil, N. and Benkacem, T. (2007) Synthesis of porous titanium dioxide membranes. *Desalination* 206(1-3), 531-537.
- Agoudjil, N., Benmouhoub, N. and Larbot, A. (2005) Synthesis and characterization of inorganic membranes and applications. *Desalination* 184(1-3), 65-69.
- Amirbahman, A., Gfeller, M. and Furrer, G. (2000) Kinetics and mechanism of ligand-promoted decomposition of the Keggin Al-13 polymer. *Geochimica Et Cosmochimica Acta* 64(5), 911-919.
- Ammary, B.Y. and Cleasby, J.L. (2004) Effect of addition sequence on dual-coagulant performance. *Journal American Water Works Association* 96(2), 90-101.
- Amy, G. and Cho, J. (1999) Interactions between natural organic matter (NOM) and membranes: Rejection and fouling. *Water Science and Technology* 40(9), 131-139.
- Aoustin, E., Schafer, A.I., Fane, A.G. and Waite, T.D. (2001) Ultrafiltration of natural organic matter. *Separation and Purification Technology* 22-3(1-3), 63-78.
- Avena, M.J. and Koopal, L.K. (1999) Kinetics of humic acid adsorption at solid-water interfaces. *Environmental Science & Technology* 33(16), 2739-2744.
- Baker, R.W. (1991) Membrane separation systems : recent developments and future directions. Baker, R.W. (ed), pp. 337-339, Noyes Data Corp., Park Ridge, N.J., U.S.A.
- Bell-Ajy, K., Abbaszadegan, M., Ibrahim, E., Verges, D. and LeChevallier, M. (2000) Conventional and optimized coagulation for NOM removal. *Journal American Water Works Association* 92(10), 44-58.
- Berube, P.R., Mavinic, D.S., Hall, E.R., Kenway, S.E. and Roett, K. (2002) Evaluation of adsorption and coagulation as membrane pretreatment steps for the removal of organic material and disinfection-by-product precursors. *Journal of Environmental Engineering and Science* 1(6), 465-476.
- Besra, L., Sengupta, D.K., Roy, S.K. and Ay, P. (2002) Polymer adsorption: its correlation with flocculation and dewatering of kaolin suspension in the presence and absence of surfactants. *International Journal of Mineral Processing* 66(1-4), 183-202.

- Bolto, B., Dixon, D., Eldridge, R. and King, S. (2001) Cationic polymer and clay or metal oxide combinations for natural organic matter removal. *Water Research* 35(11), 2669-2676.
- Bolto, B. and Gregory, J. (2007) Organic polyelectrolytes in water treatment. *Water Research* 41(11), 2301-2324.
- Bolton, G., LaCasse, D. and Kuriyel, R. (2006a) Combined models of membrane fouling: Development and application to microfiltration and ultrafiltration of biological fluids. *Journal of Membrane Science* 277(1-2), 75-84.
- Bolton, G.R., Boesch, A.W. and Lazzara, M.J. (2006b) The effects of flow rate on membrane capacity: Development and application of adsorptive membrane fouling models. *Journal of Membrane Science* 279(1-2), 625-634.
- Bottero, J.Y., Axelos, M., Tchoubar, D., Cases, J.M., Fripiat, J.J. and Fiessinger, F. (1987) Mechanism of Formation of Aluminum Trihydroxide from Keggin Al13 Polymers. *Journal of Colloid and Interface Science* 117(1), 47-57.
- Bottino, A., Capannelli, C., Del Borghi, A., Colombino, M. and Conio, O. (2001) Water treatment for drinking purpose: ceramic microfiltration application. *Desalination* 141(1), 75-79.
- Bouchard, C.R., Carreau, P.J., Matsuura, T. and Sourirajan, S. (1994) Modeling of Ultrafiltration - Predictions of Concentration Polarization Effects. *Journal of Membrane Science* 97, 215-229.
- Bouchard, C.R., Jolicoeur, J., Kouadio, P. and Britten, M. (1997) Study of humic acid adsorption on nanofiltration membranes by contact angle measurements. *Canadian Journal of Chemical Engineering* 75(2), 339-345.
- Brant, J.A. and Childress, A.E. (2002) Assessing short-range membrane-colloid interactions using surface energetics. *Journal of Membrane Science* 203(1-2), 257-273.
- Bratby, J. (2006) *Coagulation and flocculation in water and wastewater treatment*, IWA Publishing, London ;Seattle.
- Buffle, J. and Leppard, G.G. (1995) Characterization of Aquatic Colloids and Macromolecules. 1. Structure and Behavior of Colloidal Material. *Environmental Science & Technology* 29(9), 2169-2175.
- Capannelli, G., Bottino, A., Gekas, V. and Tragardh, G. (1990) Protein Fouling Behavior of Ultrafiltration Membranes Prepared with Varying Degrees of Hydrophilicity. *Process Biochemistry* 25(6), 221-224.

- Carroll, T., Booker, N.A. and Meier-Haack, J. (2002) Polyelectrolyte-grafted microfiltration membranes to control fouling by natural organic matter in drinking water. *Journal of Membrane Science* 203(1-2), 3-13.
- Carroll, T., King, S., Gray, S.R., Bolto, B.A. and Booker, N.A. (2000) The fouling of microfiltration membranes by NOM after coagulation treatment. *Water Research* 34(11), 2861-2868.
- Chang, E.E., Chiang, P.C., Tang, W.Y., Chao, S.H. and Hsing, H.J. (2005) Effects of polyelectrolytes on reduction of model compounds via coagulation. *Chemosphere* 58(8), 1141-1150.
- Chellam, S. and Cogan, N.G. (2011) Colloidal and bacterial fouling during constant flux microfiltration: Comparison of classical blocking laws with a unified model combining pore blocking and EPS secretion. *Journal of Membrane Science* 382(1-2), 148-157.
- Chen, Y., Dong, B.Z., Gao, N.Y. and Fan, J.C. (2007) Effect of coagulation pretreatment on fouling of an ultrafiltration membrane. *Desalination* 204(1-3), 181-188.
- Cheryan, M. (1998) Ultrafiltration and microfiltration handbook [electronic resource]. Cheryan, M. and NetLibrary, I. (eds), pp. xvii, 527 p., Technomic Pub. Co., Lancaster, Pa.
- Cho, J., Amy, G. and Pellegrino, J. (2000) Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. *Journal of Membrane Science* 164(1-2), 89-110.
- Cho, J.W., Amy, G., Pellegrino, J. and Yoon, Y.M. (1998) Characterization of clean and natural organic matter (NOM) fouled NF and UF membranes, and foulants characterization. *Desalination* 118(1-3), 101-108.
- Cho, M.H., Lee, C.H. and Lee, S. (2005) Influence of floc structure on membrane permeability in the coagulation-MF process. *Water Science and Technology* 51(6-7), 143-150.
- Cho, M.H., Lee, C.H. and Lee, S. (2006) Effect of flocculation conditions on membrane permeability in coagulation-microfiltration. *Desalination* 191(1-3), 386-396.
- Choi, Y.H., Kim, H.S. and Kweon, J.H. (2008) Role of hydrophobic natural organic matter flocs on the fouling in coagulation-membrane processes. *Separation and Purification Technology* 62(3), 529-534.
- Chow, C.W.K., van Leeuwen, J.A., Drikas, M., Fabris, R., Spark, K.M. and Page, D.W. (1999) The impact of the character of natural organic matter in conventional treatment with alum. *Water Science and Technology* 40(9), 97-104.

- Christensen, M. (2005) Microfiltration and ultrafiltration membranes for drinking water, American Water Works Association, Denver, CO
- Cogan, N.G. and Chellam, S. (2009) Incorporating pore blocking, cake filtration, and EPS production in a model for constant pressure bacterial fouling during dead-end microfiltration. *Journal of Membrane Science* 345(1-2), 81-89.
- Combe, C., Molis, E., Lucas, P., Riley, R. and Clark, M.M. (1999) The effect of CA membrane properties on adsorptive fouling by humic acid. *Journal of Membrane Science* 154(1), 73-87.
- Contreras, A.E., Steiner, Z., Miao, J., Kasher, R. and Li, Q.L. (2011) Studying the Role of Common Membrane Surface Functionalities on Adsorption and Cleaning of Organic Foulants Using QCM-D. *Environmental Science & Technology* 45(15), 6309-6315.
- Costa, A.R., de Pinho, M.N. and Elimelech, M. (2006) Mechanisms of colloidal natural organic matter fouling in ultrafiltration. *Journal of Membrane Science* 281(1-2), 716-725.
- Crittenden, J., Trussell, R., Hand, D., Howe, K. and Tchobanoglous, G. (2005) *Water Treatment Principles and Design*, Hoboken, N.J. : John Wiley, New Jersey.
- Davis, J.A. (1982) Adsorption of Natural Dissolved Organic-Matter at the Oxide Water Interface. *Geochimica Et Cosmochimica Acta* 46(11), 2381-2393.
- de Lara, R. and Benavente, J. (2009) Use of hydrodynamic and electrical measurements to determine protein fouling mechanisms for microfiltration membranes with different structures and materials. *Separation and Purification Technology* 66(3), 517-524.
- Dempsey, B.A. (1989) Reactions between Fulvic-Acid and Aluminum - Effects on the Coagulation Process. *Acs Symposium Series* 219, 409-424.
- DrIoli, E. and Giorno, L. (2009) Membrane operations : innovative separations and transformations. Drioli, E. and Giorno, L. (eds), pp. xxv, 551 p., Wiley-VCH, Weinheim.
- Duclos-Orsello, C., Li, W.Y. and Ho, C.C. (2006) A three mechanism model to describe fouling of microfiltration membranes. *Journal of Membrane Science* 280(1-2), 856-866.
- Elimelech, M., Zhu, X.H., Childress, A.E. and Hong, S.K. (1997) Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *Journal of Membrane Science* 127(1), 101-109.

- Ensikat, H.J. and Barthlott, W. (1993) Liquid Substitution - a Versatile Procedure for Sem Specimen Preparation of Biological-Materials without Drying or Coating. *Journal of Microscopy-Oxford* 172, 195-203.
- Fan, L.H., Harris, J.L., Roddick, F.A. and Booker, N.A. (2001) Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. *Water Research* 35(18), 4455-4463.
- Farahbakhsh, K., Svrcek, C., Guest, R.K. and Smith, D.W. (2004) A review of the impact of chemical pretreatment on low-pressure water treatment membranes. *Journal of Environmental Engineering and Science* 3(4), 237-253.
- Fiksdal, L. and Leiknes, T. (2006) The effect of coagulation with MF/UF membrane filtration for the removal of virus in drinking water. *Journal of Membrane Science* 279(1-2), 364-371.
- Fontyn, M., Vantriet, K. and Bijsterbosch, B.H. (1991) Surface Spectroscopic Studies of Pristine and Fouled Membranes .2. Method Development and Adsorption Mechanism. *Colloids and Surfaces* 54(3-4), 349-362.
- Fu, X.Y., Maruyama, T., Sotani, T. and Matsuyama, H. (2008) Effect of surface morphology on membrane fouling by humic acid with the use of cellulose acetate butyrate hollow fiber membranes. *Journal of Membrane Science* 320(1-2), 483-491.
- Furrer, G., Gfeller, M. and Wehrli, B. (1999) On the chemistry of the Keggin Al-13 polymer: Kinetics of proton-promoted decomposition. *Geochimica Et Cosmochimica Acta* 63(19-20), 3069-3076.
- Furukawa, D. (2008) A Global Perspective of Low Pressure Membranes, National Water Research Institute, Fountain Valley, CA.
- Gai, X.J. and Kim, H.S. (2008) The role of powdered activated carbon in enhancing the performance of membrane systems for water treatment. *Desalination* 225(1-3), 288-300.
- Gekas, V., Persson, K.M., Wahlgren, M. and Sivik, B. (1992) Contact Angles of Ultrafiltration Membranes and Their Possible Correlation to Membrane Performance. *Journal of Membrane Science* 72(3), 293-302.
- Gill, R.I.S. and Herrington, T.M. (1988) Floc Size Studies on Kaolin Suspensions Flocculated with Cationic Polyacrylamides. *Colloids and Surfaces* 32(3-4), 331-344.
- Goldberg, E.D., Baker, M. and Fox, D.L. (1952) Microfiltration in Oceanographic Research .1. Marine Sampling with the Molecular Filter. *Journal of Marine Research* 11(2), 194-204.



- Gonsalves, V.E. (1950) A Critical Investigation on the Viscose Filtration Process. *Recueil Des Travaux Chimiques Des Pays-Bas-Journal of the Royal Netherlands Chemical Society* 69(7), 873-903.
- Grace, H.P. (1956) Structure and Performance of Filter Media. *Aiche Journal* 2(3), 307-336.
- Grathwohl, P. (1990) Influence of Organic-Matter from Soils and Sediments from Various Origins on the Sorption of Some Chlorinated Aliphatic-Hydrocarbons - Implications on Koc Correlations. *Environmental Science & Technology* 24(11), 1687-1693.
- Gray, S.R. and Ritchie, C.B. (2006) Effect of organic polyelectrolyte characteristics on floc strength. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 273(1-3), 184-188.
- Gray, S.R., Ritchie, C.B., Tran, T. and Bolto, B.A. (2007) Effect of NOM characteristics and membrane type on microfiltration performance. *Water Research* 41(17), 3833-3841.
- Gray, S.R., Ritchie, C.B., Tran, T., Bolto, B.A., Greenwood, P., Busetti, F. and Allpike, B. (2008) Effect of membrane character and solution chemistry on microfiltration performance. *Water Research* 42(3), 743-753.
- Gregor, J.E., Nokes, C.J. and Fenton, E. (1997) Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation. *Water Research* 31(12), 2949-2958.
- Griot, O. and Kitchene.Ja (1965) ROLE OF SURFACE SILANOL GROUPS IN FLOCCULATION OF SILICA SUSPENSIONS BY POLYACRYLAMIDE .1. CHEMISTRY OF ADSORPTION PROCESS. *Transactions of the Faraday Society* 61(509P), 1026-&.
- Guell, C. and Davis, R.H. (1996) Membrane fouling during microfiltration of protein mixtures. *Journal of Membrane Science* 119(2), 269-284.
- Guo, X.Y., Li, Q.L., Hu, W.L., Gao, W. and Liu, D.F. (2009) Ultrafiltration of dissolved organic matter in surface water by a polyvinylchloride hollow fiber membrane. *Journal of Membrane Science* 327(1-2), 254-263.
- Han, B.B., Runnells, T., Zimbron, J. and Wickramasinghe, R. (2002) Arsenic removal from drinking water by flocculation and microfiltration. *Desalination* 145(1-3), 293-298.
- Han, M.J., Barona, G.N.B. and Jung, B. (2011) Effect of surface charge on hydrophilically modified poly(vinylidene fluoride) membrane for microfiltration. *Desalination* 270(1-3), 76-83.

- Hermans, P.H. and Bredee, H.L. (1935) Information on filtration laws. *Recueil Des Travaux Chimiques Des Pays-Bas* 54, 680-700.
- Hermia, J. (1982) Constant Pressure Blocking Filtration Laws - Application to Power-Law Non-Newtonian Fluids. *Transactions of the Institution of Chemical Engineers* 60(3), 183-187.
- Hilal, N., Ogunbiyi, O.O., Miles, N.J. and Nigmatullin, R. (2005) Methods employed for control of fouling in MF and UF membranes: A comprehensive review. *Separation Science and Technology* 40(10), 1957-2005.
- Hlavacek, M. and Bouchet, F. (1993) Constant Flow-Rate Blocking Laws and an Example of Their Application to Dead-End Microfiltration of Protein Solutions. *Journal of Membrane Science* 82(3), 285-295.
- Ho, C.C. and Zydney, A.L. (1999a) Effect of membrane morphology on the initial rate of protein fouling during microfiltration. *Journal of Membrane Science* 155(2), 261-275.
- Ho, C.C. and Zydney, A.L. (1999b) Theoretical analysis of the effect of membrane morphology on fouling during microfiltration. *Separation Science and Technology* 34(13), 2461-2483.
- Ho, C.C. and Zydney, A.L. (2000a) A combined pore blockage and cake filtration model for protein fouling during microfiltration. *Journal of Colloid and Interface Science* 232(2), 389-399.
- Ho, C.C. and Zydney, A.L. (2000b) Measurement of membrane pore interconnectivity. *Journal of Membrane Science* 170(1), 101-112.
- Ho, C.C. and Zydney, A.L. (2002) Transmembrane pressure profiles during constant flux microfiltration of bovine serum albumin. *Journal of Membrane Science* 209(2), 363-377.
- Hoek, E.M.V., Bhattacharjee, S. and Elimelech, M. (2003) Effect of membrane surface roughness on colloid-membrane DLVO interactions. *Langmuir* 19(11), 4836-4847.
- Hong, S.K. and Elimelech, M. (1997) Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science* 132(2), 159-181.
- Howe, K.J. and Clark, M.M. (2002) Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environmental Science & Technology* 36(16), 3571-3576.

- Howe, K.J., Marwah, A., Chiu, K.P. and Adham, S.S. (2006) Effect of coagulation on the size of MF and UF membrane foulants. *Environmental Science & Technology* 40(24), 7908-7913.
- Huang, H., Lee, N., Young, T., Gary, A., Lozier, J.C. and Jacangelo, J.G. (2007) Natural organic matter fouling of low-pressure, hollow-fiber membranes: Effects of NOM source and hydrodynamic conditions. *Water Research* 41(17), 3823-3832.
- Huang, H., Schwab, K. and Jacangelo, J.G. (2009) Pretreatment for Low Pressure Membranes in Water Treatment: A Review. *Environmental Science & Technology* 43(9), 3011-3019.
- Huang, X.H., Leal, M. and Li, Q.L. (2008) Degradation of natural organic matter by TiO<sub>2</sub> photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Research* 42(4-5), 1142-1150.
- Hundt, T.R. and Omelia, C.R. (1988) Aluminum Fulvic Acid Interactions - Mechanisms and Applications. *Journal American Water Works Association* 80(4), 176-186.
- Jang, W., Nikolov, A. and Wasan, D.T. (2004) Effect of depletion force on the stability of food emulsions. *Journal of Dispersion Science and Technology* 25(6), 817-821.
- Jarvis, P., Jefferson, B., Dixon, D. and Parsons, S.A. (2008a) Treatment options and their effect on NOM-coagulant floc structures. *Journal American Water Works Association* 100(1), 64-73.
- Jarvis, P., Jefferson, B. and Parsons, S.A. (2006) Floc structural characteristics using conventional coagulation for a high doc, low alkalinity surface water source. *Water Research* 40(14), 2727-2737.
- Jarvis, P., Parsons, S.A., Henderson, R., Nixon, N. and Jefferson, B. (2008b) The practical application of fractal dimension in water treatment practice - the impact of polymer dosing. *Separation Science and Technology* 43(7), 1785-1797.
- Jermann, D., Pronk, W. and Boller, M. (2008a) Mutual Influences between Natural Organic Matter and Inorganic Particles and Their Combined Effect on Ultrafiltration Membrane Fouling. *Environmental Science & Technology* 42(24), 9129-9136.
- Jermann, D., Pronk, W., Kagi, R., Halbeisen, M. and Boller, M. (2008b) Influence of interactions between NOM and particles on UF fouling mechanisms. *Water Research* 42(14), 3870-3878.
- Jermann, D., Pronk, W., Meylan, S. and Boller, M. (2007) Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production. *Water Research* 41(8), 1713-1722.

- Jin, B., Wilen, B.M. and Lant, P. (2003) A comprehensive insight into floc characteristics and their impact on compressibility and settleability of activated sludge. *Chemical Engineering Journal* 95(1-3), 221-234.
- Jonsson, C. and Jonsson, A.S. (1995) Influence of the Membrane Material on the Adsorptive Fouling of Ultrafiltration Membranes. *Journal of Membrane Science* 108(1-2), 79-87.
- Juang, R.S., Chen, H.L. and Chen, Y.S. (2008) Membrane fouling and resistance analysis in dead-end ultrafiltration of *Bacillus subtilis* fermentation broths. *Separation and Purification Technology* 63(3), 531-538.
- Kam, S.K. and Gregory, J. (2001) The interaction of humic substances with cationic polyelectrolytes. *Water Research* 35(15), 3557-3566.
- Kanani, D.A., Sun, X.H. and Ghosh, R. (2008) Reversible and irreversible membrane fouling during in-line microfiltration of concentrated protein solutions. *Journal of Membrane Science* 315(1-2), 1-10.
- Kang, J.S., Shim, J.K., Huh, H. and Loo, Y.M. (2001) Colloidal adsorption of bovine serum albumin on porous polypropylene-g-poly(2-hydroxyethyl methacrylate) membrane. *Langmuir* 17(14), 4352-4359.
- Karnik, B.S., Davies, S.H., Baumann, M.J. and Masten, S.J. (2005a) The effects of combined ozonation and filtration on disinfection by-product formation. *Water Research* 39(13), 2839-2850.
- Karnik, B.S., Davies, S.H., Baumann, M.J. and Masten, S.J. (2005b) Fabrication of catalytic membranes for the treatment of drinking water using combined ozonation and ultrafiltration. *Environmental Science & Technology* 39(19), 7656-7661.
- Katsoufidou, K., Yiantsios, S.G. and Karabelas, A.J. (2007) Experimental study of ultrafiltration membrane fouling by sodium alginate and flux recovery by backwashing. *Journal of Membrane Science* 300(1-2), 137-146.
- Kazpard, V., Lartiges, B.S., Frochot, C., de la Caillerie, J.B.D., Viriot, M.L., Portal, J.M., Gerner, T. and Bersillon, J.L. (2006) Fate of coagulant species and conformational effects during the aggregation of a model of a humic substance with Al-13 polycations. *Water Research* 40(10), 1965-1974.
- Kelly, S.T. and Zydney, A.L. (1994) Effects of Intermolecular Thiol-Disulfide Interchange Reactions on Bsa Fouling During Microfiltration. *Biotechnology and Bioengineering* 44(8), 972-982.
- Khan, M.M.T., Lewandowski, Z., Takizawa, S., Yamada, K., Katayama, H., Yamamoto, K. and Ohgaki, S. (2009) Continuous and efficient removal of THMs from river

- water using MF membrane combined with high dose of PAC. *Desalination* 249(2), 713-720.
- Kim, E.K. and Walker, H.W. (2001) Effect of cationic polymer additives on the adsorption of humic acid onto iron oxide particles. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 194(1-3), 123-131.
- Kim, H.C., Hong, J.H. and Lee, S. (2006) Fouling of microfiltration membranes by natural organic matter after coagulation treatment: A comparison of different initial mixing conditions. *Journal of Membrane Science* 283(1-2), 266-272.
- Kim, I.S. and Jang, N. (2006) The effect of calcium on the membrane biofouling in the membrane bioreactor (MBR). *Water Research* 40(14), 2756-2764.
- Kim, J.S., Akeprathumchai, S. and Wickramasinghe, S.R. (2001) Flocculation to enhance microfiltration. *Journal of Membrane Science* 182(1-2), 161-172.
- Kimura, K., Hane, Y., Watanabe, Y., Amy, G. and Ohkuma, N. (2004) Irreversible membrane fouling during ultrafiltration of surface water. *Water Research* 38(14-15), 3431-3441.
- Kimura, K., Yamamura, H. and Watanabe, Y. (2006) Irreversible fouling in MF/UF membranes caused by natural organic matters (NOMs) isolated from different origins. *Separation Science and Technology* 41(7), 1331-1344.
- Kochkodan, V.M., Hilal, N., Goncharuk, V.V., Al-Khatib, L. and Levadna, T.I. (2006) Effect of the surface modification of polymer membranes on their microbiological fouling. *Colloid Journal* 68(3), 267-273.
- Kothari, N. and Taylor, J.S. (1998) Pilot scale microfiltration at Manitowoc. *Desalination* 119(1-3), 93-102.
- Kulovaara, M., Metsamuuronen, S. and Nystrom, M. (1999) Effects of aquatic humic substances on a hydrophobic ultrafiltration membrane. *Chemosphere* 38(15), 3485-3496.
- Kummert, R. and Stumm, W. (1980) The Surface Complexation of Organic-Acids on Hydrated Gamma-Al<sub>2</sub>O<sub>3</sub>. *Journal of Colloid and Interface Science* 75(2), 373-385.
- Lebeau, T., Lelievre, C., Buisson, H., Cleret, D., Van de Venter, L.W. and Cote, P. (1998) Immersed membrane filtration for the production of drinking water: combination with PAC for NOM and SOC's removal. *Desalination* 117(1-3), 219-231.
- Lee, H.S., Kim, C.G. and Yoon, T.I. (2003a) Comment on "the interaction of humic substances with cationic polyelectrolytes". *Water Research* 37(3), 715-716.

- Lee, J.D., Lee, S.H., Jo, M.H., Park, P.K., Lee, C.H. and Kwak, J.W. (2000) Effect of coagulation conditions on membrane filtration characteristics in coagulation-microfiltration process for water treatment. *Environmental Science & Technology* 34(17), 3780-3788.
- Lee, N., Amy, G., Croue, J.P. and Buisson, H. (2005a) Morphological analyses of natural organic matter (NOM) fouling of low-pressure membranes (MF/UF). *Journal of Membrane Science* 261(1-2), 7-16.
- Lee, N.H., Amy, G., Croue, J.P. and Buisson, H. (2004) Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research* 38(20), 4511-4523.
- Lee, S.A., Fane, A.G., Amal, R. and Waite, T.D. (2003b) The effect of floc size and structure on specific cake resistance and compressibility in dead-end microfiltration. *Separation Science and Technology* 38(4), 869-887.
- Lee, S.Y.A., Fane, A.G. and Waite, T.D. (2005b) Impact of natural organic matter on floc size and structure effects in membrane filtration. *Environmental Science & Technology* 39(17), 6477-6486.
- Lee, W. and Westerhoff, P. (2006) Dissolved organic nitrogen removal during water treatment by aluminum sulfate and cationic polymer coagulation. *Water Research* 40(20), 3767-3774.
- Leiknes, T., Odegaard, H. and Myklebust, H. (2004) Removal of natural organic matter (NOM) in drinking water treatment by coagulation-microfiltration using metal membranes. *Journal of Membrane Science* 242(1-2), 47-55.
- Li, Q.L. and Elimelech, M. (2004) Organic fouling and chemical cleaning of nanofiltration membranes: Measurements and mechanisms. *Environmental Science & Technology* 38(17), 4683-4693.
- Li, Q.L. and Elimelech, M. (2006) Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter. *Journal of Membrane Science* 278(1-2), 72-82.
- Li, Q.L., Snoeyink, V.L., Mariaas, B.J. and Campos, C. (2003) Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. *Water Research* 37(4), 773-784.
- Li, Q.L., Xu, Z.H. and Pinnau, I. (2007) Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: Role of membrane surface properties and initial permeate flux. *Journal of Membrane Science* 290(1-2), 173-181.
- Lin, H.J., Liao, B.Q., Chen, J.R., Gao, W.J., Wang, L.M., Wang, F.Y. and Lu, X.F. (2011) New insights into membrane fouling in a submerged anaerobic membrane

- bioreactor based on characterization of cake sludge and bulk sludge. *Bioresource Technology* 102(3), 2373-2379.
- Lin, J.L., Chin, C.J.M., Huang, C.P., Pan, J.R. and Wang, D.S. (2008a) Coagulation behavior of Al-13 aggregates. *Water Research* 42(16), 4281-4290.
- Lin, S.H., Hung, C.L. and Juang, R.S. (2008b) Applicability of the exponential time dependence of flux decline during dead-end ultrafiltration of binary protein solutions. *Chemical Engineering Journal* 145(2), 211-217.
- Loh, S., Beuscher, U., Poddar, T.K., Porter, A.G., Wingard, J.M., Husson, S.M. and Wickramasinghe, S.R. (2009) Interplay among membrane properties, protein properties and operating conditions on protein fouling during normal-flow microfiltration. *Journal of Membrane Science* 332(1-2), 93-103.
- Manttari, M., Puro, L., Nuortila-Jokinen, J. and Nystrom, M. (2000) Fouling effects of polysaccharides and humic acid in nanofiltration. *Journal of Membrane Science* 165(1), 1-17.
- Maruyama, T., Katoh, S., Nakajima, M. and Nabetani, H. (2001) Mechanism of bovine serum albumin aggregation during ultrafiltration. *Biotechnology and Bioengineering* 75(2), 233-238.
- Masion, A., Thomas, F., Tchoubar, D., Bottero, J.Y. and Tekely, P. (1994) Chemistry and Structure of Al(OH)/Organic Precipitates - a Small-Angle X-Ray-Scattering Study .3. Depolymerization of the Al-13 Polycation by Organic-Ligands. *Langmuir* 10(11), 4353-4356.
- Matsui, Y., Yuasa, A., Furuya, Y. and Kamei, T. (1998) Dynamic analysis of coagulation with alum and PACl. *Journal American Water Works Association* 90(10), 96-106.
- Mavrov, V., Chmiel, H., Kluth, J., Meier, J., Heinrich, F., Ames, P., Backes, K. and Usner, P. (1998) Comparative study of different MF and UF membranes for drinking water production. *Desalination* 117(1-3), 189-196.
- McCurdy, K., Carlson, K. and Gregory, D. (2004) Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminum chloride coagulants. *Water Research* 38(2), 486-494.
- Mo, L., Huang, X. and Wu, J.L. (2002) Effect of operational conditions on membrane permeability in a coagulation-microfiltration process for water purification. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 37(2), 273-285.
- Moon, J., Kang, M.S., Lim, J.L., Kim, C.H. and Park, H.D. (2009) Evaluation of a low-pressure membrane filtration for drinking water treatment: pretreatment by coagulation/sedimentation for the MF membrane. *Desalination* 247(1-3), 271-284.

- Moulder, M. (2003) *Basic Principles of Membrane Technology*, Kluwer Academic Publishers.
- Mpofu, P., Addai-Mensah, J. and Ralston, J. (2003) Investigation of the effect of polymer structure type on flocculation, rheology and dewatering behaviour of kaolinite dispersions. *International Journal of Mineral Processing* 71(1-4), 247-268.
- Mueller, J. and Davis, R.H. (1996) Protein fouling of surface-modified polymeric microfiltration membranes. *Journal of Membrane Science* 116(1), 47-60.
- Munir, C. (1998) *The Use of Membrane Filtration in Conjunction with Coagulation Processes for Improved Nom Removal*, Lancaster, Pa. : Technomic Pub. Co., c1998.
- Nakamura, K. and Matsumoto, K. (2006) Properties of protein adsorption onto pore surface during microfiltration: Effects of solution environment and membrane hydrophobicity. *Journal of Membrane Science* 280(1-2), 363-374.
- Nasser, M.S. and James, A.E. (2006) The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions. *Separation and Purification Technology* 52(2), 241-252.
- Nozic, D.J., Freese, S.D. and Thompson, P. (2001) Longterm experience in the use of polymeric coagulants at Umgeni Water. *Water Science and Technology: Water Supply* 1(1), 43-50.
- O'Melia, C.R., Becker, W.C. and Au, K.K. (1999) Removal of humic substances by coagulation. *Water Science and Technology* 40(9), 47-54.
- Oh, J.I. and Lee, S.H. (2005) Influence of streaming potential on flux decline of microfiltration with in-line rapid pre-coagulation process for drinking water production. *Journal of Membrane Science* 254(1-2), 39-47.
- Palecek, S.P., Mochizuki, S. and Zydney, A.L. (1993) Effect of Ionic Environment on Bsa Filtration and the Properties of Bsa Deposits. *Desalination* 90(1-3), 147-159.
- Park, P.K., Lee, C.H. and Lee, S. (2006a) Permeability of collapsed cakes formed by deposition of fractal aggregates upon membrane filtration. *Environmental Science & Technology* 40(8), 2699-2705.
- Park, P.K., Lee, C.H. and Lee, S. (2006b) Variation of specific cake resistance according to size and fractal dimension of chemical flocs in a coagulation-microfiltration process. *Desalination* 199(1-3), 213-215.
- Park, P.K., Lee, C.H. and Lee, S. (2007) Determination of cake porosity using image analysis in a coagulation-microfiltration system. *Journal of Membrane Science* 293(1-2), 66-72.



- Pelekani, C., Newcombe, G., Snoeyink, V.L., Hepplewhite, C., Assemi, S. and Beckett, R. (1999) Characterization of natural organic matter using high performance size exclusion chromatography. *Environmental Science & Technology* 33(16), 2807-2813.
- Peng, S.F. and Wu, C. (1999) Light scattering study of the formation and structure of partially hydrolyzed poly(acrylamide)/calcium(II) complexes. *Macromolecules* 32(3), 585-589.
- Peng, W.H., Escobar, I.C. and White, D.B. (2004) Effects of water chemistries and properties of membrane on the performance and fouling - a model development study. *Journal of Membrane Science* 238(1-2), 33-46.
- Pikkarainen, A.T. and Judd, S.J. (2005) Errata to "Pre-coagulation for microfiltration of an upland surface water" (vol 38, pg 455, 2004). *Water Research* 39(7), 1424-1424.
- Porcelli, N. and Judd, S. (2010) Chemical cleaning of potable water membranes: A review. *Separation and Purification Technology* 71(2), 137-143.
- Ramesh, A., Lee, D.J. and Lai, J.Y. (2007) Membrane biofouling by extracellular polymeric substances or soluble microbial products from membrane bioreactor sludge. *Applied Microbiology and Biotechnology* 74(3), 699-707.
- Ramesh, A., Lee, D.J., Wang, M.L., Hsu, J.P., Juang, R.S., Hwang, K.J., Liu, J.C. and Tseng, S.J. (2006) Biofouling in membrane bioreactor. *Separation Science and Technology* 41(7), 1345-1370.
- Rana, D., Matsuura, T., Narbaitz, R.M. and Feng, C. (2005) Development and characterization of novel hydrophilic surface modifying macromolecule for polymeric membranes. *Journal of Membrane Science* 249(1-2), 103-112.
- Riedl, K., Girard, B. and Lencki, R.W. (1998) Influence of membrane structure on fouling layer morphology during apple juice clarification. *Journal of Membrane Science* 139(2), 155-166.
- Rubio, J. and Kitchener, J.A. (1976) MECHANISM OF ADSORPTION OF POLY(ETHYLENE OXIDE) FLOCCULANT ON SILICA. *Journal of Colloid and Interface Science* 57(1), 132-142.
- Sakol, D. and Konieczny, K. (2004) Application of coagulation and conventional filtration in raw water pretreatment before microfiltration membranes. *Desalination* 162(1-3), 61-73.
- Saravia, F., Zwiener, C. and Frimmel, F.H. (2006) Interactions between membrane surface, dissolved organic substances and ions in submerged membrane filtration. *Desalination* 192(1-3), 280-287.

- Schafer, A.I., Fane, A.G. and Waite, T.D. (1998) Nanofiltration of natural organic matter: Removal, fouling and the influence of multivalent ions. *Desalination* 118(1-3), 109-122.
- Schafer, A.I., Fane, A.G. and Waite, T.D. (2000a) Fouling effects on rejection in the membrane filtration of natural waters. *Desalination* 131(1-3), 215-224.
- Schafer, A.I., Schwicker, U., Fischer, M.M., Fane, A.G. and Waite, T.D. (2000b) Microfiltration of colloids and natural organic matter. *Journal of Membrane Science* 171(2), 151-172.
- Semmens, M.J. and Field, T.K. (1980) Coagulation: experiences in organic removal. *Journal American Water Works Association* 72(4), 76-83.
- Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. (2006a) Impact of fractional character on the coagulation of NOM. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 286(1-3), 104-111.
- Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. (2006b) The impact of zeta potential on the physical properties of ferric-NOM flocs. *Environmental Science & Technology* 40(12), 3934-3940.
- Sharp, E.L., Parsons, S.A. and Jefferson, B. (2004) The effects of changing NOM composition and characteristics on coagulation performance, optimisation and control. *Water Science and Technology: Water Supply* 4(4), 95-102.
- Shi, B.Y., Wei, Q.S., Wang, D.S., Zhu, Z. and Tang, H.X. (2007) Coagulation of humic acid: The performance of preformed and non-preformed Al species. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 296(1-3), 141-148.
- Smithpalmer, T., Campbell, N., Bowman, J.L. and Dewar, P. (1994) Flocculation Behavior of Some Cationic Polyelectrolytes. *Journal of Applied Polymer Science* 52(9), 1317-1325.
- Sombatsompop, K., Visvanathan, C. and Ben Aim, R. (2006) Evaluation of biofouling phenomenon in suspended and attached growth membrane bioreactor systems. *Desalination* 201(1-3), 138-149.
- Susanto, H. and Ulbricht, M. (2005) Influence of ultrafiltration membrane characteristics on adsorptive fouling with dextrans. *Journal of Membrane Science* 266(1-2), 132-142.
- Taniguchi, M., Kilduff, J.E. and Belfort, G. (2003) Low fouling synthetic membranes by UV-assisted graft polymerization: monomer selection to mitigate fouling by natural organic matter. *Journal of Membrane Science* 222(1-2), 59-70.

- Tarleton, E.S. and Wakeman, R.J. (1994) Understanding Flux Decline in Cross-Flow Microfiltration .3. Effects of Membrane Morphology. *Chemical Engineering Research & Design* 72(A4), 521-529.
- Taylor, M.L., Morris, G.E., Self, P.G. and Smart, R.S. (2002) Kinetics of adsorption of high molecular weight anionic polyacrylamide onto kaolinite: The flocculation process. *Journal of Colloid and Interface Science* 250(1), 28-36.
- Treffrygoatley, K., Buijs, K.R., Bindoff, A.M. and Buckley, C.A. (1987) The Cross-Flow Microfiltration of Problematic Surface and River Waters to Produce Potable Water. *Desalination* 67, 439-453.
- Tsuyuhara, T., Hanamoto, Y., Miyoshi, T., Kimura, K. and Watanabe, Y. (2010) Influence of membrane properties on physically reversible and irreversible fouling in membrane bioreactors. *Water Science and Technology* 61(9), 2235-2240.
- van de Ven, W.J.C., van't Sant, K., Punt, I.G.M., Zwijnenburg, A., Kemperman, A.J.B., van der Meer, W.G.J. and Wessling, M. (2008) Hollow fiber dead-end ultrafiltration: Influence of ionic environment on filtration of alginates. *Journal of Membrane Science* 308(1-2), 218-229.
- van der Marel, P., Zwijnenburg, A., Kemperman, A., Wessling, M., Temmink, H. and van der Meer, W. (2010) Influence of membrane properties on fouling in submerged membrane bioreactors. *Journal of Membrane Science* 348(1-2), 66-74.
- Vickers, J.C., Thompson, M.A. and Kelkar, U.G. (1995) The Use of Membrane Filtration in Conjunction with Coagulation Processes for Improved Nom Removal. *Desalination* 102(1-3), 57-61.
- Vrijenhoek, E.M., Hong, S. and Elimelech, M. (2001) Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. *Journal of Membrane Science* 188(1), 115-128.
- Wang, D.S., Sun, W., Xu, Y., Tang, H.X. and Gregory, J. (2004) Speciation stability of inorganic polymer flocculant-PACl. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 243(1-3), 1-10.
- Wang, J., Guan, J., Santiwong, S.R. and Waite, T.D. (2008) Characterization of floc size and structure under different monomer and polymer coagulants on microfiltration membrane fouling. *Journal of Membrane Science* 321(2), 132-138.
- Wang, S., Li, Q. and Liu, C. (2010) Fouling of Microfiltration Membranes by Organic Polymer Coagulants and Flocculants: Controlling Factors and Mechanisms. *Water Research In Press, Accepted Manuscript*.

- Wang, S., Liu, C. and Li, Q. (2011) Fouling of microfiltration membranes by organic polymer coagulants and flocculants: Controlling factors and mechanisms. *Water Research* 45(1), 357-365.
- Wei, J.C., Gao, B.Y., Yue, Q.Y., Wang, Y., Li, W.W. and Zhu, X.B. (2009) Comparison of coagulation behavior and floc structure characteristic of different polyferric-cationic polymer dual-coagulants in humic acid solution. *Water Research* 43(3), 724-732.
- Wu, X.H., Ge, X.P., Wang, D.S. and Tang, H.X. (2007) Distinct coagulation mechanism and model between alum and high Al-13-PACl. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 305(1-3), 89-96.
- Xu, R. (2002) Particle characterization: light scattering methods Kluwer Academic Publishers, New York.
- Yamamura, H., Kimura, K., Okajima, T., Tokumoto, H. and Watanabe, Y. (2008) Affinity of functional groups for membrane surfaces: Implications for physically irreversible fouling. *Environmental Science & Technology* 42(14), 5310-5315.
- Yamamura, H., Kimura, K. and Watanabe, Y. (2007) Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment. *Environmental Science & Technology* 41(19), 6789-6794.
- Yan, M.Q., Wang, D.S., Ni, J.R., Qu, J.H., Chow, C.W.K. and Liu, H.L. (2008a) Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics. *Water Research* 42(13), 3361-3370.
- Yan, M.Q., Wang, D.S., Yu, J.F., Ni, J.R., Edwards, M. and Qu, H.H. (2008b) Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation. *Chemosphere* 71(9), 1665-1673.
- Ye, Y., Le Clech, P., Chen, V. and Fane, A.G. (2005) Evolution of fouling during crossflow filtration of model EPS solutions. *Journal of Membrane Science* 264(1-2), 190-199.
- Yeh, H.M. and Wu, H.H. (1997) Membrane ultrafiltration in combined hollow-fiber module systems. *Journal of Membrane Science* 124(1), 93-105.
- Yuan, W., Kocic, A. and Zydney, A.L. (2002) Analysis of humic acid fouling during microfiltration using a pore blockage-cake filtration model. *Journal of Membrane Science* 198(1), 51-62.
- Yuan, W. and Zydney, A.L. (1999a) Effects of solution environment on humic acid fouling during microfiltration. *Desalination* 122(1), 63-76.

- Yuan, W. and Zydney, A.L. (1999b) Humic acid fouling during microfiltration. *Journal of Membrane Science* 157(1), 1-12.
- Yuan, W. and Zydney, A.L. (2000) Humic acid fouling during ultrafiltration. *Environmental Science & Technology* 34(23), 5043-5050.
- Zator, M., Ferrando, M., Lopez, F. and Guell, C. (2009) Microfiltration of protein/dextran/polyphenol solutions: Characterization of fouling and chemical cleaning efficiency using confocal microscopy. *Journal of Membrane Science* 344(1-2), 82-91.
- Zhang, M.M., Li, C., Benjamin, M.M. and Chang, Y.J. (2003) Fouling and natural organic matter removal in adsorben/membrane systems for drinking water treatment. *Environmental Science & Technology* 37(8), 1663-1669.
- Zhao, Y.Q. (2004) Settling behaviour of polymer flocculated water-treatment sludge II: effects of floc structure and floc packing. *Separation and Purification Technology* 35(3), 175-183.
- Zhou, Y. and Franks, G.V. (2006) Flocculation mechanism induced by cationic polymers investigated by light scattering. *Langmuir* 22(16), 6775-6786.
- Ziegmann, M., Saravia, F., Torres, P.A. and Frimmel, F.H. The hybrid process TiO<sub>2</sub>(2)/PAC: performance of membrane filtration. *Water Science and Technology* 62(5), 1205-1212.
- Zularisam, A.W., Ismail, A.F., Salim, M.R., Sakinah, M. and Ozaki, H. (2007) The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes. *Desalination* 212(1-3), 191-208.
- Zularisam, A.W., Ismail, A.F. and Salim, R. (2006) Behaviours of natural organic matter in membrane filtration for surface water treatment - a review. *Desalination* 194(1-3), 211-231.
- Zydney, A.L. and Ho, C.C. (2003) Effect of membrane morphology on system capacity during normal flow microfiltration. *Biotechnology and Bioengineering* 83(5), 537-543.